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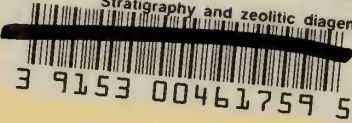
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Stratigraphy and zeolitic diagenesis



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STRATIGRAPHY AND
ZEOLITIC DIAGENESIS OF THE
JOHN DAY FORMATION OF OREGON

BY
RICHARD L. HAY

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STRATIGRAPHY AND ZEOLITIC DIAGENESIS OF THE JOHN DAY FORMATION OF OREGON

BY

RICHARD L. HAY

ABSTRACT

The 3,000-foot John Day Formation near Mitchell, Oregon, consists largely of massive tuffaceous claystones, vitric tuffs, and rhyolitic ignimbrite of Late Oligocene and Early Miocene age. The upper and lower members of the formation are dominantly an air-laid accumulation of dacitic and rhyolitic ash, much of which weathered to montmorillonite at the land surface before burial. The middle member is a compound rhyolitic ignimbrite.

Two sharply separated mineralogic facies occur within the John Day Formation. Clinoptilolite replaces vitric material in most claystones and tuffs of the lower part of the formation, termed the *clinoptilolite facies*, whereas fresh glass is present and zeolite is absent in the upper part of the formation, termed the *fresh glass facies*. The clinoptilolite facies can be subdivided into a montmorillonite subfacies and a celadonite subfacies on the basis of clay-mineral content. Field relationships indicate that zeolitic diagenesis was accomplished during or after folding of the John Day Formation but prior to extrusion of the Middle Miocene Columbia River Basalt. Petrographic relationships indicate that most clinoptilolite replacements of vitric particles were formed by precipitation of the zeolite within pseudomorphic cavities from which the glass had been dissolved. Opal, orthoclase, and celadonite were locally co-precipitated with clinoptilolite. Nearly all the montmorillonite preceded the zeolite with which it is associated, as most of the celadonite may have done, but calcite was deposited after the zeolite. Chalcedony, fluorapatite, vermiculite, and kaolinite are among the other authigenic minerals found in the clinoptilolite facies.

The formation of clinoptilolite from rhyolitic glass involves principally a gain of H₂O and Ca and losses of Si, Na, and K. Exchange of ions by dacitic and rhyolitic beds in the process of zeolitic diagenesis resulted in gains of Fe, Ti, Mg, Ca, and P by rhyolitic beds and gains of K and Si by some, at least, of the dacitic beds.

The subsurface water responsible for zeolitic diagenesis in the John Day Formation originated as meteoric water which acquired an increasing pH and an increasing concentration of dissolved species in passing downward and laterally through beds of the formation. Clinoptilolite probably crystallized initially near the base of the formation, where the pH and concentration of ions were presumably highest. Once crystallization of clinoptilolite had begun, the solution should have become increasingly undersaturated with respect to glass, which should now have dissolved at an accelerated rate. Clinoptilolite should have continued to crystallize until all the glass had dissolved or until changed subsurface conditions were encountered. This process could account for the pattern of zeolitic diagenesis, the sharpness of the transition between the clinoptilolite facies and the fresh glass facies, and the complete zeolitic replacement of glass usually found in beds of the clinoptilolite facies. Metastable nucleation may account for the authigenic vermiculite, kaolinite, and most of the authigenic orthoclase.

INTRODUCTION

THE JOHN DAY FORMATION forms the middle unit in a column of Tertiary non-marine volcanic rocks roughly 5,000–10,000 feet thick in the area mapped, which lies at the southern margin of the Columbia Plateau (fig. 1). Nearly everywhere at the base of this sequence is the Eocene–Early Oligocene (?) Clarno Formation, mostly lava flows and volcanic breccias, which ranges from 0 to 5,000 feet thick. The John Day Formation, of Late Oligocene and Early Miocene age, consists largely of silicic tuffs and tuffaceous claystones, but locally contains flows of olivine basalt. It is separated from the Clarno Formation by an angular uncon-

formity on which a weathered profile is nearly everywhere developed. Where the Clarno Formation is absent, the John Day Formation overlies conglomerates and sandstones of Cretaceous age. The thickness of the John Day Formation ranges from about 1,300 feet to 3,000 feet in the area mapped. Soon after it was deposited, it was warped into northeast-southwest-trending folds, which were deeply eroded prior to outpouring of the Middle Miocene Columbia River Basalt. The Columbia

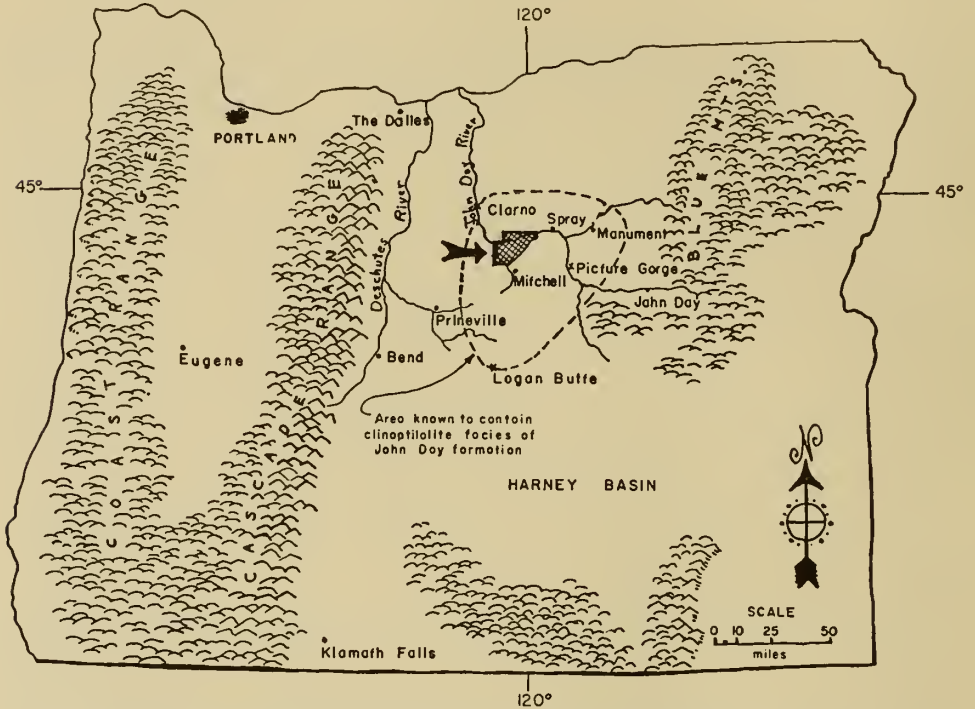


Fig. 1. Index map of Oregon, showing known extent of clinoptilolite facies of the John Day Formation. Arrow indicates area studied in detail (see fig. 2, in pocket).

River Basalt flows, at least 2,500 feet thick, have been faulted and deformed into broad basins and arches whose long axes trend northeast-southwest.

The Tertiary formations illustrate three different types of zeolite occurrence. The Clarno Formation contains heulandite, laumontite, stilbite, and a wide variety of other zeolites of hydrothermal origin, as well as a much smaller amount of diagenetic clinoptilolite. The John Day Formation contains clinoptilolite and heulandite formed diagenetically at low temperatures over a broad area. Late magmatic or deuteric chabazite, thomsonite, and analcite are abundant in some of the thicker Columbia River Basalt flows. The present study is concerned only with the regional zeolitic diagenesis in the John Day Formation.

Diagenetic alteration of pyroclastic deposits to zeolites has been widely recognized for several decades, and it now seems clear that several factors control the nature of zeolitic diagenesis. Coombs (1954) in a classic study was able to relate the occurrence of analcite, heulandite, and laumontite to different burial depths,

and in this case the pressure and temperature of burial seem to have determined whether laumontite or analcite and heulandite were formed. By contrast, water composition seems to exercise a controlling influence on the nature of the zeolites formed at low temperatures and shallow depths (cf. Ross, 1928; Bradley, 1929). The present paper is concerned with the regional alteration of volcanic glass at depths of less than 4,000 feet, where solution chemistry seems to have controlled the pattern of alteration and the minerals formed.

The John Day Formation was studied in moderate detail during the summers of 1956 and 1958–1961 over an area of about 200 square miles (fig. 2, in pocket) which lies to the north and northeast of Mitchell (fig. 1). Reconnaissance was also made of an additional 1,500 square miles, outlined by the dashed line in figure. Approximately 17,000 feet of beds were measured and described. Much of this stratigraphic information is given here, as it provides the basis for several conclusions about the pattern and mechanism of zeolitic diagenesis.

For this study, 400 thin sections of rocks were examined, and 160 diffractometer patterns were made either of bulk samples or of size and mineral fractions. Chemical analyses were obtained from twenty-two rock samples and three mineral samples in order to determine the chemical composition of the rocks of the John Day Formation and the chemical changes produced by diagenesis. The sand-size fractions of eight disaggregated samples were magnetically separated into fractions which were sieved in order to determine the size distribution of crystals and rock fragments.

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STRATIGRAPHY

THE CLARNO FORMATION

The Clarno Formation consists largely of lava flows and volcanic breccias, but volcanic conglomerates and sandstones, claystones, and vitric tuffs are common in some places. The various lithologic facies interfinger laterally, and no units have been found which are sufficiently widespread to subdivide the formation satisfactorily over a distance of more than 10 miles. The full thickness of the formation is about 5,000 feet, measured by the writer in and near the southwest

part of the mapped area (fig. 2); it has been entirely eroded only 10 miles to the northeast, where the John Day Formation overlies Cretaceous beds.

The lower 4,300–4,500 feet of the measured section consists mainly of calc-alkaline andesitic lavas and fragmental deposits of varied texture. These rocks have been hydrothermally altered to varying degrees, and a wide variety of minerals has been formed. Veins of coarse heulandite, stilbite, and laumontite are common in the lower 1,500 feet of the formation, and broad alteration haloes in the adjacent country rock contain albite, laumontite, heulandite, chlorite, and montmorillonite. Hydrothermal alteration decreases upward, and is locally evident only in the uppermost 1,000 feet of this lower part of the formation.

The uppermost 500–700 feet of the Clarno Formation comprise rhyolitic lavas, varicolored kaolinitic claystones, conglomerates, and rhyolitic vitric tuffs without evidence of hydrothermal alteration. Vitric material is, however, replaced by clinoptilolite, montmorillonite, and opal of probable diagenetic origin throughout a sequence of rhyolitic tuff beds as much as 50 feet thick which is interbedded with lava flows and claystones over an area of 5 square miles in the NE $\frac{1}{4}$ T. 11 S., R. 20 E. Pinkish-orange clinoptilolite locally cements rhyodacite autoclastic breccia 200–300 feet thick at the base of the large lava dome forming Sheep Mountain, in the NE $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 28, T. 11 S., R. 20 E.

Leaves and seeds collected from several horizons in the Clarno Formation have long been accepted as Eocene (e.g., Scott, 1954), although more recently Hergert (1961) proposed an Oligocene age for some plant materials. Mammal remains from a bed 50 feet thick below the unconformity at the top of the formation near Clarno (fig. 1) are considered to be latest Eocene or earliest Oligocene by Malcolm McKenna (1959, personal communication).

Potassium-argon dates of 36 and 37 million years were obtained from the uppermost part of the formation near Mitchell. The 37 m.y. date was given by a bulk sample of pyroxene andesite collected near the center SW $\frac{1}{4}$ sec. 8, T. 11 S., R. 21 E., from a 100-foot flow which lies about 100 feet above the base of a 400-foot series of flows forming the uppermost unit of the Clarno Formation. The date of 36 m.y. was given by sanidine from a 20-foot crystal-rich bentonitic claystone which underlies the 400-foot series of andesite flows. The dated sample was collected near SE cor. sec. 2, T. 11 S., R. 20 E. These dates are most likely to be early Oligocene, judging from the age of Eocene and Oligocene fossiliferous strata which have been dated by the potassium-argon method (Curtis and Evernden, 1962, personal communication).

UNCONFORMITY AT THE BASE OF THE JOHN DAY FORMATION

The unconformity at the base of the John Day Formation was a deeply weathered land surface on which hills of resistant rock stood as much as 300 feet above the lowland areas. Overlying the residual weathered profile, 10–50 feet thick, is a discontinuous red colluvial deposit, 10–20 feet thick, which is derived from the residual profile. Kaolinite or halloysite $\cdot 2\text{H}_2\text{O}$ is the principal clay mineral both in the residual profile and in the colluvial deposit above. Descriptions of this surface have been given elsewhere by Waters *et al.* (1951) and Hay (1962*a*).

THE JOHN DAY FORMATION

The John Day Formation is a conformable sequence, subdivided here into three members on the basis of a widespread rhyolitic ignimbrite which lies near the middle of the formation. The beds below the ignimbrite constitute the lower member, which is largely tuffaceous claystone and silicic vitric tuff. The rhyolite ignimbrite forms the middle member, as defined here, and the upper member, like the lower, consists mostly of silicic tuffs and tuffaceous claystones. This subdivision should not be confused with that of Merriam (1901), in which color is one of the principal characters used in subdividing the formation into three members. Most of the characters used by Merriam vary laterally and serve to define lithologic facies rather than widespread members of the vertical sequence. The following description of the formation can be supplemented by the reports of Merriam (1901), Calkins (1902), Coleman (1949a), Fisher and Wilcox (1960), and Hay (1962a).

Lower member.—The thickness of the lower member is 1,135 feet in the one complete but composite section which was measured (Hay, 1962a, fig. 2). This is probably a maximum, and the member is presumably as much as 300 feet thinner in some places, for the unconformity at the base of the John Day Formation has a local relief of 300 feet. Tuffaceous claystones form about three-quarters of the member, on the average, and most of the remainder is vitric tuff, either primary or reworked.

a) Tuffaceous claystone. All the claystones examined are tuffaceous, containing recognizable pyroclastic material, either fresh or altered. They form massive, poorly defined beds which appear uniform through thicknesses of a few feet to 20 or more feet and which weather to smooth slopes or badland topography. Most are red (reddish-brown or grayish-red), but others are pale brown, light olive-gray, or green. Montmorillonite is the only clay mineral in the yellow claystone, whereas the red ones contain both montmorillonite and kaolinite (or halloysite $\cdot 2\text{H}_2\text{O}$). Most green claystones contain both montmorillonite and celadonite. Red claystones form the basal bed of the formation and in some places occur nearly continually through the lower 450 feet or more. These can be distinguished from the colluvial claystones which conformably underlie the John Day Formation by the presence of plagioclase and the predominance of montmorillonite over kaolinite.

Most or all of the yellow and green claystones were originally 85–90 per cent vitric material. Pumice fragments, either fresh or altered, are the most common type of vitric particle, but shards can usually be identified. Altered pumice of the claystone is poorly sorted; most particles range between 0.25 mm and 1 mm in length, but fragments as long as 4 mm occur in many beds. Zeolitized or fresh vitric material (principally shards¹) is present in nearly all the claystones from the upper 550–650 feet of the member and in only about a third of the claystones

¹ The term *shard* is applied here to fragments of glass which retain some of the original, usually curved, surface of one or more vesicles. The definition excludes angular fragments of massive obsidian. This restriction of the term *shard* is supported by current usage (Petitjohn, 1957, p. 336; Swineford *et al.*, 1955).

below, where most of the volcanic glass has been altered to montmorillonite. Refractive index of the unaltered glass is uniformly 1.500–1.502 ± .002.

Sand-sized euhedral or broken crystals (principally plagioclase) and rock fragments (largely silicic lava) form 3–13 per cent of the massive claystones and as much as 50 per cent of the small sandy lenses which were disaggregated and sieved. Andesine is the principal feldspar and may occur alone or together with oligoclase or labradorite, or both. Sanidine was identified in about a third of the claystones, and it predominates in a very few. Ferromagnesian minerals usually form a few tenths of 1 per cent of the claystones and invariably include magnetite and ilmenite. Pyroxene, hornblende, or biotite, or any combination of these were found in most claystones sampled in the upper 550–650 feet of the lower member but in only a few of those below. The abundant crystals of andesine suggest an original dacitic composition of most claystones, but the refractive index of the unaltered glass ($n = 1.500\text{--}1.502$) would seem to indicate a rhyolitic or rhyodacitic magma (cf. George, 1924). Separate sources for glass and crystals need not be considered, however; glass having a refractive index of 1.502 was found adhering to the andesine (An_{42}) crystals in one sample. The refractive index of the dacitic glass has probably been lowered by postdepositional hydration and possibly also by leaching. Rhyolitic, rhyodacitic, and andesitic eruptions contributed lesser materials to the claystones (Hay, 1962a).

Structures reflecting exposure of the claystones at the land surface before burial are widespread through the member and are particularly common in the lower 350 feet of the formation. Most abundant of these structures are clay-filled root cavities in the claystones and animal burrowings (?) in the tuffs (Hay, *ibid.*).

b) Vitric tuffs. Vitric tuffs resulting from ash falls on the land surface form evenly stratified, well-indurated beds a few inches to 10 feet thick at intervals through the entire thickness of the lower member. Most tuffs are medium- to coarse-grained, but lapilli tuff is not rare, and a few beds of fine-grained tuff have been noted. Nearly all the tuffs contain a matrix of montmorillonite, and all gradations exist between tuffs and tuffaceous claystones. Pumice fragments as much as 4 mm long are present in most tuffs, and fragments 1 cm long occur in several beds. Feldspar crystals and rock fragments usually form 5–10 per cent of the tuffs. Sanidine equals or exceeds plagioclase (chiefly oligoclase and sodic andesine) in at least half of the tuffs; sodic andesine or oligoclase is common and sanidine is rare or absent in the others. Although quartz is rare in most tuffs, it is rather common in a few. Pyroxene, either fresh or altered, generally is present but never forms as much as 1 per cent of a bed. The sanidine-rich tuffs are thought to be rhyolitic; those in which plagioclase is the dominant feldspar are more likely to be rhyodacitic or dacitic.

Two of the sanidine-rich tuffs were traced laterally into thinly bedded, rather well-sorted reworked tuff, and reworked tuffs form a thinly bedded facies which interfingers with massive claystones at several horizons in the lower 240 feet of the member (Hay, 1962a).

A single massive tuff bed as much as 25 feet thick was deposited as an ash flow. Crystals of sanidine, plagioclase, and quartz suggest a rhyolitic composition for the tuff, which is locally welded and devitrified (SW cor. sec. 15, T. 9 S., R. 21 E.).

This ignimbrite was found only in the northwestern part of the area mapped (fig. 4, in pocket), where it lies within 50 feet of the base of the formation. It appears to be the same ignimbrite which forms the basal bed of the formation in the vicinity of Clarno, 15 miles to the northwest.

Among the air-laid tuffs, one rhyolitic bed deserves special mention because of its broad extent and distinctive lithology. This coarse sanidine-rich tuff, 1–3 feet thick, lies 500–835 feet above the base of the formation and ranges from 200 to 400 feet below the ignimbrite forming the middle member of the John Day Formation. Where extensively reworked, the tuff may attain a thickness of 30 feet.

The crystals of sanidine are 1–4 mm in average diameter and have a composition of $\text{Or}_{43}\text{Ab}_{54}\text{An}_{3}$, based on a complete chemical analysis (Hay, 1962*b*). Myrmekitic intergrowths of quartz and sanidine mantle many of the sanidine crystals. This bed may be the ash-fall equivalent of an ignimbrite near Ashwood, 25 miles to the northwest, which contains abundant myrmekite-mantled crystals of sodic sanidine (Peck, 1961). If this correlation is correct, then most of the 4,000-foot section of ignimbrites, lavas, and tuffs measured near Ashwood by Peck would seem to be equivalent to the lower member of the John Day Formation near Mitchell.

c) Olivine basalt. Flows of olivine basalt are widespread in the lower 250 feet of the member and occur through most of its thickness in Donnely Basin (fig. 2, in pocket), where eight flows totaling about 400 feet are well exposed. Individual flows are 30–100 feet thick, and one bed of basaltic agglomerate is 30 feet thick. A feeder dike in Donnely Basin was reported by Lindsley (1961), and another was noted in the present work. Texture of the basalt varies from coarse-grained and ophitic to medium-grained and intergranular. All the lavas contain an estimated 5–15 per cent olivine, part of which is unaltered. The pyroxene in the coarse-grained basalt is a pinkish-brown, presumably titaniferous augite. Interstitial alkali feldspar was identified in five of the nine thin sections, and phlogopitic (?) biotite was seen in three of them. Chemical analyses given by Lindsley (1961, p. 137, nos. 13, 14) and Hay (1962*a*, no. 6) indicate that the basalt is alkaline and undersaturated.

The lower seven flows of the John Day Formation in Donnely Basin have been assigned to the Clarno Formation by Lindsley, but several facts argue against this interpretation:

1. The basalt flows conformably underlie tuffs and claystones of the John Day Formation. No evidence could be found to support Lindsley's belief that an unconformity separates these basalts from the tuffs and claystones. Furthermore, a weathered profile is lacking over the surface of the basalt flows, unlike the top of the Clarno Formation where it has been mapped by the writer. These basalts are the oldest rocks exposed in Donnely Basin; hence their relationships to the underlying beds cannot be seen.

2. Reworked tuffs and tuffaceous claystones similar to those of the John Day Formation are interbedded with the lavas. Similar beds are lacking in the Clarno Formation where it has been studied by the writer.

3. The olivine basalt flows are fresher than those of the Clarno Formation within the area of figure 2 (in pocket).

4. The olivine basalts of the John Day Formation are alkaline, undersaturated lavas quite different in mineral and chemical composition from the oversaturated calc-alkaline lavas characteristic of the Clarno Formation. The chemical analysis of a flow which Lindsley (1961, p. 137, no. 13) considers to be part of the Clarno Formation is almost a perfect duplicate of the analysis of a flow he accepts as part of the John Day Formation (p. 137, no. 14). Their chemical similarity supports the present writer's opinion that both should be included within the John Day Formation.

Middle member.—The middle member of the John Day Formation is a widespread compound rhyolitic ignimbrite ranging from 12 feet to about 250 feet thick. Its average thickness is 120 feet, based on eleven complete measured sections of the deposit. The ignimbrite exhibits all gradations between nonporous, highly welded tuff and porous, friable lapilli tuff in which the particles of glass are neither flattened by compaction nor welded. Two flow units can usually be seen, and three units are recognizable in a few places. Only the lower parts of the flow units are welded, and the degree of compaction and the welding are greatest where the units are thickest. Welded and semiwelded tuff of the upper flow units is generally devitrified² to a lithoidal rock where the units are thickest; the basal flow unit is nowhere devitrified. The ignimbrite is commonly underlain by a few feet of thinly bedded vitric tuff and lapilli tuff mineralogically similar to the ignimbrite. This tuff is evidently the deposit of one or more ash falls which preceded the ignimbrite.

The complete sequence of flow units is represented by the ignimbrite of figure 8, section 9 (in pocket). The basal unit, 25–50 feet thick, is unwelded lapilli tuff with coarse black shards, pumice blocks as much as 3 inches long, and abundant fragments of black, densely welded vitric tuff $\frac{1}{4}$ of an inch to 2 inches in average diameter. The middle unit, about 80 feet thick, comprises 40 feet of columnar-jointed, devitrified welded tuff underlain and overlain by claystone formed by alteration of unwelded vitric ignimbrite. The welded tuff contains blocks of pumice as much as 10 inches long and devitrified blocks of rhyolitic glass as much as 3 inches in average diameter. The uppermost unit, 15 feet thick, is devitrified semiwelded tuff in which the coarsest fragments of pumice are 2 inches long and the coarsest fragments of devitrified glass are 5 mm in average diameter. Unwelded tuff was probably eroded from the surface of the uppermost unit before the succeeding beds were deposited, judging from the usual occurrences of unwelded tuff above devitrified and semiwelded tuff.

The uppermost flow unit is present wherever the appropriate stratigraphic interval is exposed in the western half of the area mapped (fig. 4, in pocket). The middle unit is more restricted, and the lower unit still more restricted in its distribution. These areal relationships suggest that the first two flow units filled pre-existing valleys, and the upper flow unit spread widely over an even land surface. In the area to the east (fig. 5, in pocket) two flow units were recognized which resemble the middle and upper units of the western area.

The three flow units are similar in mineral composition. The modal composition of fresh, densely welded tuff averaged from two thin sections is as follows: glass

² The term *devitrified* is used in this paper only to describe glass of pyroclastic origin which has crystallized to alkali feldspar and cristobalite.

(fresh or devitrified), 97.4 per cent; crystals (principally plagioclase), 1.5 per cent; rock fragments (almost exclusively rhyolite), 1.0 per cent; all other material, 0.1 per cent. Oligoclase (chiefly An₁₀₋₁₂) is the dominant feldspar,³ but crystals of sanidine, andesine, and labradorite have been identified. Most samples contain a few crystals of broken or euhedral quartz and of fresh or altered iron-rich clinopyroxene ($n_z = 1.762 \pm .003$). A few "iddingsite" pseudomorphs after euhedral (fayallitic?) olivine have been seen. Refractive index of the densely welded vitric tuff

TABLE 1

MOLECULAR NORMS OF VITRIC AND DEVITRIFIED IGIMBRITE FROM THE JOHN DAY FORMATION

Normative minerals	1	2	3	4	5
Q.....	32.2	31.6	33.9	33.8	32.5
Or.....	30.5	25.0	23.5	36.5	20.0
Ab.....	30.0	34.5	36.0	25.5	40.5
An.....	3.0	4.0	2.5	2.5	2.0
Co.....	0.2	0.4	1.5	0.7	2.6
Hy.....	2.2	2.6	0.6	0.2	0.4
Ilm.....	0.4	0.4	0.2	...	0.2
Hm.....	1.5	0.2	1.7
Mt.....	1.2	1.2
Ru.....	0.2	0.3	0.1
Ap.....	0.3	0.3	0.3	0.3	...
Sum of ferromagnesian minerals.....	4.1	4.5	2.8	1.0	2.4
Normative anorthite content.....	9.1	11.0	6.5	9.0	5.0

NOTE: Explanation of column numbers.

1. Glass from fragments of densely welded vitric tuff (table 7, no. 1).
2. Densely welded vitric tuff (table 7, no. 2).
3. Devitrified densely welded tuff (table 7, no. 3).
4. Moderately porous semiwelded devitrified tuff (table 7, no. 4).
5. Fragments of devitrified glass (table 7, no. 5).

and of the shards in unwelded tuff is $1.504 \pm .002$. Alkali feldspar and alpha cristobalite can be recognized in diffractometer patterns of the devitrified glass, and both albite and a nearly pure potash feldspar were identified by immersion methods in the more coarsely devitrified glass. Chemical analyses of relatively unaltered ignimbrite are listed in table 7, nos. 1-5, and the norms are given in table 1. The major differences in chemical composition are believed to reflect postdepositional changes rather than magmatic differences (see p. 236).

The ignimbrite near Mitchell is the same one that is conspicuously exposed at Picture Gorge, 30 miles to the east (fig. 1), which generally comprises two flow units similar in thickness, lithology, and stratigraphic position to the upper two units near Mitchell. Coleman's detailed description (1949*a*) leaves little doubt that this ignimbrite at Picture Gorge is mineralogically similar to the ignimbrite near Mitchell.

³ Plagioclase compositions given in this report were determined from both n_x and n_z , using the high-temperature curves of Smith (1958). Determinations are considered accurate within 3 per cent anorthite content.

Upper member.—The upper member is at least 1,300 feet thick at one place where the exposures are excellent (fig. 4, sec. 10) and is probably 400 feet thicker where the greatest thickness seems to be preserved (fig. 4, sec. 13). This member is thin or absent where the formation was uplifted and deeply eroded prior to the Columbia River Basalt (cf. fig. 4, sec. 6; fig. 5, secs. 17–20). Claystones and tuffs form about 95 per cent and conglomerates and sandstones about 5 per cent of the measured sections indicated on figures 4 and 5 (in pocket).

a) *Tuffaceous claystones and vitric tuff.* The claystones and tuffs forming the bulk of the upper member are massive, poorly sorted, fine- to medium-grained beds of rather uniform texture, composition, and color. Most of these beds are similar to those forming the upper 550–650 feet of the lower member, except for differences related to zeolitic diagenesis. These rocks are characteristically yellowish-gray or light olive gray.

Feldspar crystals and fragments of volcanic rock form 5–10 per cent of most claystones and tuffs; the remainder consists of fresh or altered vitric material—principally shards and pumice. All gradations exist between tuffs and claystones, and many rocks are difficult to classify accurately in the field. Most tuffs are resistant and form rounded ledges; claystones characteristically weather to smooth slopes or badland topography. Many beds of tuff and claystone are extensively penetrated by root cavities or small animal burrows. Beds penetrated in this fashion may occur singly, or they may form a continuous sequence as much as 40 feet thick.

The principal feldspar is andesine, which forms broken and euhedral crystals; sanidine and quartz are rare or absent. Refractive index of the glass shards ranges from 1.496 to $1.502 \pm .002$, suggesting a silicic composition, and most rock fragments are of silicic lava. Clinopyroxene and magnetite are the dominant ferromagnesian minerals, and smaller amounts of ilmenite, hornblende, and biotite are often present. Ferromagnesian minerals rarely if ever total as much as 1 per cent of the rocks. Most of the pyroclastic material in these tuffs and claystones, like that of the claystones in the lower member, is thought to have originated in dacitic eruptions.

A few beds of coarse rhyolitic tuff and coarse tuffaceous claystone which may contain abundant oligoclase are present in the lower 500 feet of the upper member. One of these, rich in shards of black obsidian ($n = 1.500$) as much as 5 mm long, is a discontinuous but widespread bed which lies about 300 feet above the base of the upper member. The scarcity of sanidine in rhyolitic tuffs of the upper member contrasts sharply with its common occurrence in rhyolitic tuffs of the lower member.

b) *Reworked tuffs and conglomerates.* Reworked tuffs and conglomerates interfinger with massive tuffs and claystones at many places in the upper member. The reworked tuffs vary from rather poorly sorted, massive beds to well-sorted, thin-bedded or cross-bedded ones. The reworked tuffs contain rounded grains of tuff in addition to the same kinds of pyroclastic material found in the adjacent tuffs and claystones. Individual beds of reworked tuff and conglomerate are lenticular, and a few of the conglomerates fill steep-walled stream channels, one of which has slopes of 65° and a depth of about 30 feet. Pebbles and small cobbles of tuff eroded

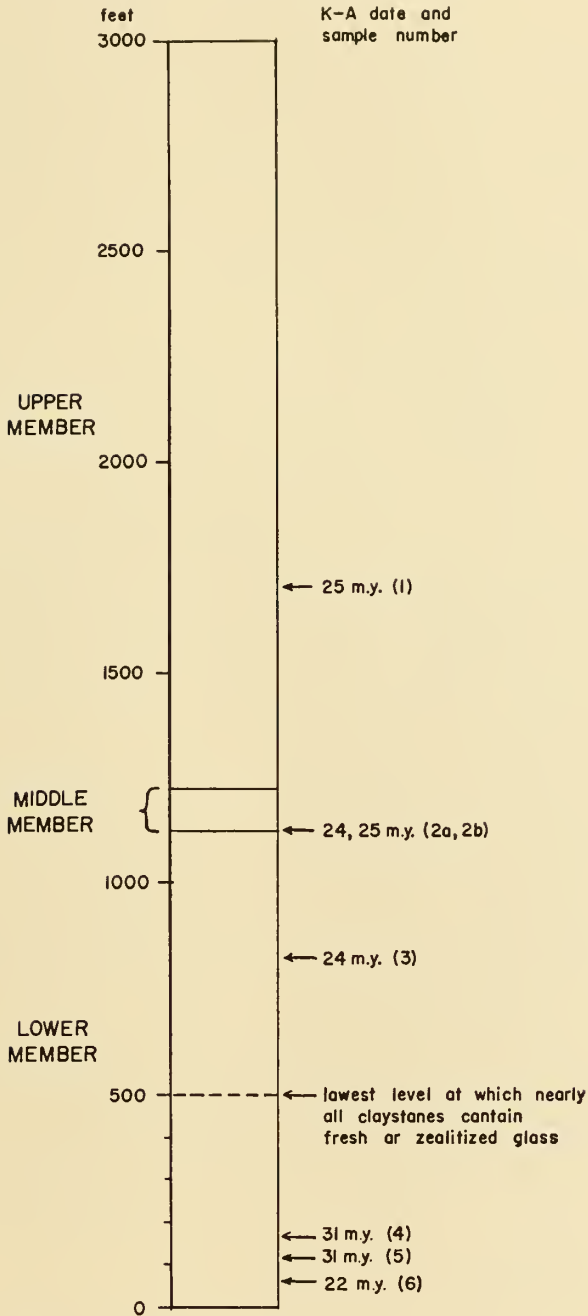


Fig. 3. K-A dates and stratigraphic positions of dated materials in the John Day Formation. Locations of dated materials given in Hay (1962a). All dates represent pyrogenic materials except no. 6, which was obtained from authigenic orthoclase. The inaccurate stratigraphic position for sample no. 1 given earlier (Hay, 1962a) is corrected here.

from the upper member are most abundant in the conglomerates, but there are a few beds of subangular fragments of welded tuff, and others of well-rounded pebbles and cobbles of welded tuff and andesite (esp. sec. 11, fig. 2, in pocket).

Age and origin.—The John Day Formation is a conformable sequence comprising Upper Oligocene and Lower Miocene beds. The basal part of the lower member is thought to be Upper Oligocene on the basis of a well-preserved flora (Chaney, 1952) and the jaw of an *Archaeotherium* sp. (Coleman, 1949b). Lower Miocene vertebrate fossils constituting the well-known John Day fauna are both widespread and abundant in the upper one-half to two-thirds of the lower member, as defined here, and throughout the upper member (Wood *et al.*, 1941).

Two potassium-argon dates of 31 m.y. were given by pyrogenic materials from the lower 165 feet of the formation, and dates of 24–25 m.y. were obtained from samples at distances of 835, 1,110, and about 1,700 feet above the base of the formation (fig. 3). The sample collected 835 feet above the base gives an age of 24 m.y., and that collected about 865 feet higher gives an age of 25 m.y., but the apparent contradiction between K-A age and stratigraphic position is probably not significant, as analytical errors in the age determination may total 5 per cent, representing about a million years. If these dates are accepted as accurate within 1 million years, then the lower 835 feet represent a time span of about 7 million years, and the 865 feet of overlying beds accumulated during a million years or less.

Both the lower and upper members are mostly deposits of air-laid ash on the land surface. Subaerial structures such as root cavities and animal burrows are present at many levels in both members, and pahoehoe structure was noted in a lava flow. Size distribution of the crystals and rock fragments in most beds suggests that the ash fell directly from eruptive clouds at a considerable distance from the source volcanoes (Hay, 1962a). Most of the massive, fine- to medium-grained deposits of the upper and lower members are thought to have formed by the accumulation of thin deposits of ash at infrequent intervals; reworking of the surficial layers of ash by roots, burrowing organisms, and sheet wash eliminated the initial stratification and produced the massive bedding characteristic of these deposits. Most reworked tuffs of the lower member are lacustrine, but those of the upper member were deposited by streams.

Lithologic features and potassium-argon dates leave little doubt that most or all of the claystones in the lower 450 feet of the formation were formed by weathering at the land surface before burial. Clay-filled root cavities, montmorillonite pseudomorphs after plagioclase, and desiccation cracks in claystones with vitroclastic textures are among the features which imply weathering (Hay, 1962a). The average sedimentation rate (about 0.1 of a foot per 1,000 years for the lower 835 feet of the formation) should have been sufficiently slow for most of the glass to weather to clay (Hay, 1960).

Claystones of the ignimbrite member appear to have formed after burial. Zeolite-free claystone may grade upward into less-altered ignimbrite, which is the reverse order of that found in the soil profile, where the surface layers are the most highly weathered. Evidence of surface exposure (root markings, burrowings, etc.) is lacking in the ignimbrite, although as much as 100 feet of claystone have been measured in one place, and thicknesses of 20–30 feet are common. Claystone and

lapilli tuff intergrade laterally over short distances within the ignimbrite, in contrast to the extensive beds of root-marked claystone formed by weathering in the lower 450 feet of the formation. Sharp lateral transitions between some thin beds of tuff and equivalent claystone seem to favor a diagenetic origin for these claystones, as with those of the ignimbrite.

The relative roles of weathering and diagenesis in forming montmorillonite are difficult to assess in the remaining three-quarters or more of the formation. An average sedimentation rate on the order of 1 foot per 1,000 years seems possible for the tuffs and claystones 835–1,700 feet above the base of the formation, judging from the potassium-argon dates. This rate seems compatible with weathering of a considerable amount of glass to montmorillonite in a seasonally humid climate (Hay, 1960). The lateral continuity of most claystones above and below the ignimbrite and root markings in many of these beds can be used as evidence that the claystones formed by weathering. Petrographic relations given on page 214 show that some montmorillonite was formed diagenetically in the matrix of rocks which now contain clinoptilolite, although few claystones other than those of the ignimbrite may have originated in this way.

The presence of pre-John Day hills is shown locally through the lower 240 feet of the formation by the pattern of lithologic facies and the presence of dome-shaped mantles (Hay, 1962*a*, fig.4). The hills were probably eliminated as topographic features by the time the lower 350 feet of the formation had been deposited, and the beds above accumulated on a rather level plain traversed by small streams.

Volcanoes in the vicinity of the present Cascade Range, 90–100 miles to the west, are thought to have supplied most of the pyroclastic material in the lower and upper members of the John Day Formation. Large volumes of dacite, andesite, and rhyodacite pyroclastic material were discharged from vents there during the Oligocene and early Miocene (Peck, 1960), and andesine phenocrysts predominate in these Cascade dacites, just as crystals of andesine do in the John Day Formation. The hilly weathered surface of the Clarno Formation supplied the red kaolinic clay which colors many claystones in the lower 450 feet of the formation.

The coarse sanidine tuffs of the lower member probably originated from the rhyolitic vents 10–25 miles to the west which were reported by Waters (1954) and Peck (1961). The ignimbrite near the base of the formation (fig. 4, in pocket) thickens to the northwest and has been traced within 15 miles of Ashwood; it could easily have issued from one of these rhyolitic vents. The ignimbrite forming the middle member could also have originated from these rhyolitic vents, although supporting evidence is lacking.

UNCONFORMITY AT THE TOP OF THE JOHN DAY FORMATION

The angular unconformity at the top of the John Day Formation was an uneven land surface cut in the relatively soft tuffs and claystones forming the upper member and at one place into those of the lower member of the John Day Formation. This gently rolling to hilly surface was dissected by steep-walled valleys not uncommonly a few hundred feet deep. The maximum local relief is about 1,000 feet, measured in Donnelly Basin from the bottom of a deep valley to the nearby

upland surface (fig. 5, in pocket). A colluvial deposit, 5–50 feet thick, mantles the valley walls and hillslopes eroded in the upper surface of the formation. This deposit is commonly a massive breccia of tuff blocks 1–16 inches across in a matrix of clayey tuff or tuffaceous claystone. Neither the colluvium nor the eroded upper surface of the John Day Formation seems to be deeply weathered.

THE COLUMBIA RIVER BASALT

The Columbia River Basalt is represented by as much as 2,500 feet of basalt flows and minor interbedded basaltic pyroclastic deposits. The full thickness originally present is unknown, as the top has been eroded. These basalts are divisible in the field into a lower series of ophitic flows totaling 300–1,500 feet and an upper series of nonophitic flows about 1,000 feet thick. The great variation in thickness of the ophitic series reflects the uneven surface over which these flows were deposited.

The contact between ophitic and nonophitic flows was taken as a datum to which measured sections of the John Day Formation were referred (figs. 4, 5). One thick flow, traceable for at least 13½ miles, closely parallels the contact between ophitic and nonophitic flows over this distance (fig. 4), suggesting that the contact is a stratigraphic horizon which can be relied upon as a datum plane. This flow could not be recognized in the sections to the east (fig. 5).

Few of the ophitic flows are less than 100 feet thick, several are as much as 300 feet thick, and one flow locally attains a thickness of 350–400 feet. Ophitic textures may characterize only 5–10 feet of the thinner flows, whereas the thicker flows may be almost entirely ophitic.

The thicker ophitic flows contain late magmatic or deuteric pegmatoid veins and irregular segregations in which coarse crystals of chabazite, thomsonite, and analcite are intergrown with plagioclase, pyroxene, and olivine. Thomsonite, philipsite, and chabazite may line or fill vesicles in the same and in different flows, and apophyllite and analcite have been found in a few veins. Whether these vesicle fillings and veins were formed during or after cooling of the lava is not apparent from field relationships.

Both ophitic and nonophitic basalts in the area near Mitchell are considered equivalent to those at Picture Gorge, and they would be termed the Picture Gorge Basalt in Waters' subdivision of the Columbia River Basalt (1961). At Picture Gorge these flows are conformably overlain by the Mascall Formation, which is transitional Middle-Upper Miocene (Downs, 1956; Chaney, 1959, pp. 119–134). Much additional information concerning the flows exposed in Donnelly Basin is given by Lindsley (1961).

FIELD RELATIONSHIPS AND AGE OF ZEOLITIC DIAGENESIS

DISTRIBUTION OF DIAGENETIC FACIES

Two sharply separated mineralogic facies are present within the John Day Formation. Clinoptilolite replaces vitric material in most claystones and tuffs of the lower half of the formation, and heulandite occurs in many of the basalt flows interbedded with the zeolitic claystones and tuffs. Opal, orthoclase, celadonite, and montmorillonite are among the authigenic (i.e., postdepositional) minerals com-

monly associated with the zeolites. The upper part of the formation contains fresh glass, diagenetic montmorillonite, and a very little opal, but lacks zeolites, orthoclase, and celadonite. The rocks characterized by clinoptilolite and heulandite will be termed the *clinoptilolite facies*; those with fresh glass will be termed the *fresh glass facies*. The term *facies* is used informally here to designate these two groups of rocks having characteristic mineral contents. In the nomenclature of diagenetic

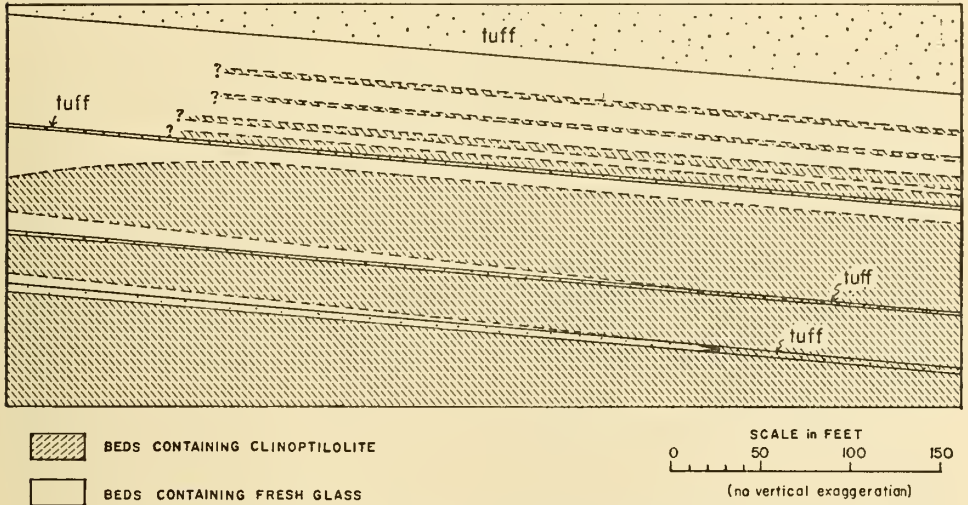


Fig. 6. Interfingering of clinoptilolite facies and fresh glass facies in area represented in fig. 4 (NE¼SE¼ sec. 13, T. 10 S., R. 20 E.). Contact between diagenetic facies indicated by dashed lines; tuff beds and claystones separated by solid lines.

mineral facies, the clinoptilolite facies of the John Day Formation probably represents the heulandite-analcite facies as defined by Paekham and Crook (1960).

The clinoptilolite facies of the John Day Formation has been observed by the writer from Clarno south to Logan Butte (fig. 1), a north-south distance of 70 miles, and as far east as Monument, for an east-west distance of 50 miles. Thomas (1956) mentions the occurrence of zeolites in the John Day Formation southeast of Ritter, about 20 miles east of Monument, thus suggesting that the clinoptilolite facies extends at least 70 miles in an east-west direction. These exposures represent an area of about 2,200 square miles. Zeolitic beds extend to the top of the formation near Clarno and at the south end of the Picture Gorge, unlike most of the area near Mitchell.

The boundary between the clinoptilolite facies and the fresh glass facies in the area of figure 2 is a somewhat uneven surface which cuts across stratigraphic horizons in the John Day Formation where it was folded prior to the Columbia River Basalt (figs. 4, 5). This boundary crudely parallels the bedding within the Columbia River Basalt and has been displaced along post-basalt faults (fig. 4, sec. 11). The surface of alteration appears to have a maximum relief of about 900 feet, relative to the top of the ophitic basalts taken as a datum in figures 4 and 5, but the variation in level is considerably less in each of the areas represented separately by these figures.

The transition between the clinoptilolite facies and the fresh glass facies may follow a single stratigraphic horizon over distances of as much as three miles, but elsewhere the transition may be a zone of interfingering (fig. 4, secs. 4, 7). Where the interfingering is complex and well exposed (fig. 6), the medium- to coarse-grained rhyolitic tuffs, which are relatively permeable, may be unaltered where the dacitic claystones above and below are zeolitic. Interfingering within the claystones does not bear any visible relation to composition, texture, or permeability.

Obvious differences in permeability have locally controlled the pattern of alteration within the ignimbrite and basalt flows. Relatively impermeable welded vitric tuff is replaced by clinoptilolite and montmorillonite only adjacent to veins of opal and clinoptilolite filling fractures which were presumably open channels at the time of alteration. The thickness of welded tuff replaced by zeolite and montmorillonite adjacent to veins may range from 1 mm to about 5 cm. Interfingering of fresh and zeolitized vitric ignimbrite may occur where wide differences in lateral permeability exist, with the more permeable ignimbrite selectively altering. Within olivine basalts, heulandite is common in vesicular zones at tops of the flows, but it is lacking in the dense, nonvesicular parts of the flows, presumably because of their low permeability.

A few beds of average permeability below the surface of the clinoptilolite facies were found to contain fresh glass and to lack clinoptilolite. The thickest of these unaltered beds is a flow unit of unwelded ignimbrite, 20–50 feet thick, which lies 200 or more feet below the surface of zeolitic alteration (fig. 8, sec. 9, in pocket). This bed contains fresh glass only where it underlies a devitrified welded tuff, and it is zeolitized where the welded tuff pinches out. Two rhyolitic tuffs interbedded with claystone in the lower 230 feet of the formation were each found to contain fresh glass and lack zeolite at one locality (SW cor. NE $\frac{1}{4}$ sec. 15; SE cor. NE $\frac{1}{4}$ sec. 16, T. 11 S., R. 20 E.). There appear to be no mineralogic or textural differences between zeolitized and unzeolitized parts of any one of these beds, except for differences produced by zeolitic diagenesis.

The transition between the clinoptilolite facies and the fresh glass facies is sharp and generally occurs through a cavernous zone, 2 mm to 2 cm thick, in which vitric particles are represented by unfilled pseudomorphous cavities in a dusky yellow groundmass which contains 30–50 per cent more montmorillonite than does the adjacent rock containing particles of fresh glass. Vitric particles adjacent to the cavernous zone are partly dissolved, and only small etched remnants of the original shards and pumice fragments may remain (pl. 2, *a*). For as much as a foot distant from the cavernous zone of contact the finest shards and pumice may be totally dissolved, whereas the coarsest shards are only etched. On the zeolitized side of the cavernous zone, clinoptilolite thinly coats the cavities from which shards and pumice have been dissolved, and the amount of cavity-filling zeolite becomes progressively greater through a distance of a few millimeters to a few centimeters from the zone. In one exceptional case, within the ignimbrite, grayish-orange spheroids of zeolitic alteration 1–3 inches across lie within the zone of fresh glass at a distance of as much as 6 inches from the prevailing contact with zeolitized ignimbrite.

In the ignimbrite, where the vitric particles vary greatly in size, the rock is not always uniformly zeolitized. Nearly all fragments of obsidian greater than a centimeter across are incompletely altered, even where all the finer material is zeolitized; and clinoptilolite was noted in diffractometer patterns of the fine groundmass of a few ignimbrite samples in which the coarse shards are etched but otherwise unaltered.

AGE AND DEPTH OF ZEOLITIC ALTERATION

The clinoptilolite faeies truncates folded beds of the John Day Formation at two places (figs. 4, 5), suggesting that the beds were altered after they were folded. If

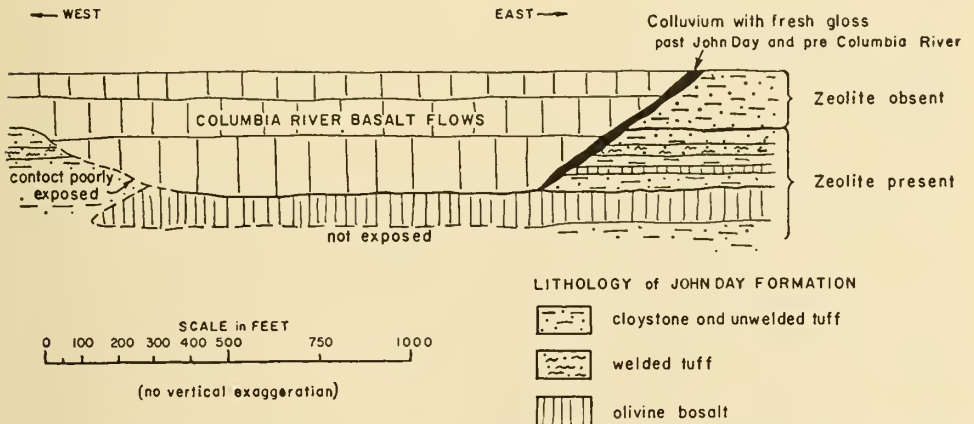


Fig. 7. Lower part of a valley cut in beds of the John Day Formation and filled with Columbia River Basalt flows. Colluvium mantling valley wall at right is a clayey tuff containing fresh glass and lacking zeolite. It lies adjacent to zeolitic claystones of the John Day Formation, thus proving that zeolitic alteration preceded the colluvium, as well as the Columbia River Basalt flows. This exposure is on north side of Donnelly Basin (fig. 2; NW cor. sec. 21, T. 9 S., R. 23E.).

the clinoptilolite had been formed before the beds were folded, this pattern could have been produced only if the original surface of zeolitic alteration in two places had been abnormally low relative to stratigraphic horizons in the John Day Formation. Later folding would have raised the two areas to approximate coincidence with the surface of alteration elsewhere—a most unlikely occurrence. The pattern of devitrification in the ignimbrite bears no spatial relation to folds or to zeolitic alteration, supporting the writer’s view that the ignimbrite devitrified at the land surface, while it was still hot.

Zeolitic alteration seems to have preceded the Columbia River Basalt, for colluvium with fresh glass mantles the sides of a basalt-filled valley cut in the clinoptilolite faeies of the John Day Formation (fig. 7). Here the colluvium is clayey tuff derived from the fresh glass faeies of the John Day Formation and is texturally similar to the adjacent zeolitic claystone and tuff. The colluvium would contain clinoptilolite rather than fresh glass if the zeolite had been formed after the colluvium and succeeding basalts had been deposited. Furthermore, the Columbia River Basalt flows filling the valley lack the heulandite which lines cavities in olivine basalt flows within the clinoptilolite faeies of the John Day Formation, including the flow which underlies the basalt-filled valley.

Authigenic orthoclase and celadonite give potassium-argon dates suggesting early zeolitic diagenesis and lending some support to the time of alteration as inferred from field relationships. Orthoclase collected 65 feet above the base of the formation gives an age of 22 m.y. (Hay, 1962a), which, based upon duplicate analyses of argon as well as potassium, should have an error of less than 5 per cent. Celadonite from the analyzed concretions of the ignimbrite (table 7, no. 10) gives an age of 24 m.y. \pm 10 per cent (Obradovich, 1962, personal communication). These dates suggest that the celadonite and orthoclase are older than the Columbia River Basalt, of Middle Miocene age, but they cannot be considered sufficiently accurate to prove whether the dated minerals were formed during or shortly after accumulation of the upper member of the John Day Formation.

The clinoptilolite facies locally lies as much as 1,250 feet below the eroded upper surface of the formation (fig. 4), and here the zeolite at the top of the clinoptilolite facies could not have formed at depths less than 1,250 feet. The depth may originally have been greater, as an unknown amount has been eroded from the top of the formation after zeolitic diagenesis. Whether the clinoptilolite now found at and near the eroded upper surface of the formation (fig. 5, secs. 17-20) was formed nearer the surface than 1,250 feet cannot be proved or disproved, in view of the unknown thickness of beds eroded prior to the extrusion of the Columbia River Basalt. The maximum depth at which clinoptilolite could have been formed in the John Day Formation was the original thickness of the formation, which was at least 3,000 feet near Mitchell and about 4,000 feet twenty miles to the west (Peck, 1961). The John Day Formation may have exceeded 3,000 feet near Mitchell, as the top seems everywhere eroded, but 4,000 feet seems to be a reasonable maximum figure, thus setting maximum burial limits of 3,000-4,000 feet for zeolitic alteration at the base of the formation.

LITHOLOGIC DESCRIPTION OF DIAGENETIC FACIES

SUBDIVISIONS OF CLINOPTILOLITE FACIES

The clinoptilolite facies of the John Day Formation can be subdivided in the field into two groups of rocks which differ in their clay-mineral content. Celadonite and montmorillonite typify one group, which will be termed the *celadonite subfacies*; by contrast, montmorillonite and kaolinite are the only clay minerals present in more than trace amounts in the other group, which will be termed the *montmorillonite subfacies*. Celadonite was nowhere found in the lower 500 feet of the formation, but the montmorillonite subfacies and celadonite subfacies interfinger laterally in the beds above (fig. 8). The celadonite subfacies seems to constitute most of the clinoptilolite facies which is exposed in the area represented by figure 5, and the montmorillonite subfacies predominates in the area of figure 4.

Observed contacts between the two subfacies follow bedding planes and may be either sharp or gradational. In a few places the contact is a zone 6 inches thick in which celadonite-free and celadonite-rich masses are irregularly distributed, giving the rock a mottled appearance.

Laterally equivalent beds of the montmorillonite and celadonite subfacies are similar in primary composition, texture, and structures, and the beds of both sub-

TABLE 2
MINERALOGIC COMPARISON OF EQUIVALENT BEDS IN DIFFERENT DIAGENETIC FACIES
OF THE JOHN DAY FORMATION

Materials compared	Clinoptilolite facies		Fresh glass facies
	Montmorillonite subfacies	Celadonite subfacies	
Glass shards	Replaced by clinoptilolite, often accompanied by opal in tuffs and ignimbrite.	Replaced by clinoptilolite; opal generally lacking except in ignimbrite.	Generally etched.
Pumice	Replaced by clinoptilolite, montmorillonite, opal.	Replaced by clinoptilolite, celadonite, montmorillonite. Opal locally present in ignimbrite.	Some appears unaltered; others replaced by montmorillonite, with or without opal.
Calcic plagioclase	Commonly replaced by orthoclase in lower 350 feet of formation; elsewhere, orthoclase replacement is rare.	Commonly replaced by orthoclase through entire thickness; rarely replaced by clinoptilolite or heulandite.	Unaltered.
Iron-rich clinopyroxene	Replaced by montmorillonite.	Etched but otherwise unaltered.	Replaced by montmorillonite.
Opal	Generally present in ignimbrite and tuffs; generally absent in claystones.	Often present in ignimbrite; generally absent in tuffs and claystones.	Occurs locally in ignimbrite; generally absent elsewhere.
Celadonite	May be present in trace amounts.	Commonly replaces vitric material, especially pumice.	Absent.
Calcite	Widespread in small amounts; concretions rare.	Widespread in moderate amounts; concretions common.	Widespread in small amounts; concretions locally common.

facies appear to have formed from similar materials by the same processes in the same type of environment.

Montmorillonite subfacies.—Tuffs of the montmorillonite subfacies are generally hard, relatively impermeable beds which weather white and may be grayish-yellow (5Y8/4)⁴, yellowish-gray (5Y8/1), or white on fresh surfaces. The coarser vitric particles are replaced principally by clinoptilolite, and the finer-grained particles and highly porous pumice are altered to montmorillonite, which forms 35–45 per cent of the tuffs examined in thin section (pl. 1). A clinoptilolite cement

⁴ Color designations refer to the Rock Color Chart of the National Research Council, 1948.

is often present, and calcareous concretions were noted in the tuffs at a few places. Several tuffs were traced laterally into montmorillonite claystones.

Most claystones of the montmorillonite subfacies are dusky yellow (5Y6/4) and have either a waxy or an earthy luster. Clinoptilolite pseudomorphic after shards is present in nearly all the claystones more than 450 feet above the base of the formation, with reference to the thickest sections, and it is present in only about a third of those in the lower 450 feet. Siliceous concentrations 1–2 feet across with cores of opalized pumice are rather common in the claystones formed from ignimbrite in Donnelly Basin, and a few calcareous concretions are associated with the siliceous ones.

Veins, principally of calcite, opal, or gypsum, are not rare in claystones and tuffs of the montmorillonite subfacies, and a little secondary calcite is disseminated in some of these rocks. Other mineralogic data are summarized in table 2.

Celadonite subfacies.—Tuffs of the celadonite subfacies are hard, relatively impermeable beds which are grayish-green (10G5/2) to pale olive (10Y6/2) on both fresh and weathered surfaces. The coarser vitric particles are replaced principally by clinoptilolite, and most of the finer-grained particles and highly porous pumice are altered to form a clay matrix consisting of about equal proportions of celadonite and montmorillonite. Clay matrix generally forms 35–45 per cent of the tuffs, and a cement of clinoptilolite is usually present.

The claystones are grayish-green to light olive-gray (5Y6/1) and may appear waxlike or have an earthy luster. Celadonite and montmorillonite form roughly equal proportions of the greenest claystones, but the light olive-gray claystones contain very little celadonite. Clinoptilolite is invariably present in the celadonitic claystones.

Concretions, cavity fillings, and disseminated crystals and aggregates of calcite are common in tuffs and claystones of the celadonite subfacies. The concretions are generally 3–6 inches across and may be concentrated in nests or layers, or they may be dispersed randomly throughout a sequence of beds. Calcite concretions almost always contain a smaller percentage of celadonite and are a paler green than are the equivalent nonconcretionary rocks. Bright grayish-green (10G4/2) celadonite-rich concretions 1–4 cm across are present in much of the celadonitic ignimbrite.

FRESH GLASS FACIES

Tuffs of the fresh glass facies form semiconsolidated to moderately indurated yellowish-gray (5Y7/2 to 5Y8/1) beds. The matrix, where present, is of montmorillonite and finely divided glass, and the montmorillonite forms an estimated 25–35 per cent of those beds which are equivalent to tuffs of the clinoptilolite facies containing 35–45 per cent clay minerals. Claystones are usually yellowish-gray (5Y7/2) or grayish-yellow (5Y8/4), and most of them have an earthy luster. Both tuffs and claystones, although relatively impermeable, appear somewhat more porous and permeable than those of the clinoptilolite facies. Unaltered vitric material is common in about 80 per cent of the claystones examined, and is absent or rare in the others.

Vitric particles are pitted by solution (etched) in about half of the samples studied with the binocular microscope, and the margins of brown glass shards are

often colorless (bleached) as seen in thin section. Highly porous, thin-walled pumice is typically altered to waxlike pink montmorillonite in tuffs and claystones and in the ignimbrite is either altered to montmorillonite or silicified.

Calcareous concretions 3–12 inches across are relatively common, and are randomly dispersed in most areas, but locally form layers. Disseminated crystals and aggregates of calcite are present in about a quarter of the thin sections examined.

Beds of the fresh glass facies stratigraphically equivalent to those of the clinoptilolite facies (fig. 8, in pocket) resemble the zeolitic beds in all lithologic aspects related to the environment and processes of sedimentation. Therefore the present lithologic differences must reflect different postdepositional environments and processes.

MICROSCOPIC PETROGRAPHY OF CLINOPTILOLITE FACIES

REPLACEMENT OF GLASS

Petrographic evidence indicates that the clinoptilolite replacing glass shards and the walls of pumice fragments was formed by crystallization of zeolite in cavities from which the glass had already been dissolved. Some of the clinoptilolite replacements of coarse fragments of glass were formed in the same way, but in other replacements the zeolite was probably deposited *pari passu* with solution of the glass. Opal, orthoclase, and celadonite were locally precipitated from solution, as was the montmorillonite of amygdules. Most or all of the montmorillonite replacing vitric material could have been formed in place by the leaching of glass.

Shards.—Shards are typically replaced by clinoptilolite, with or without opal, and there may also be small amounts of calcite, celadonite, or chalcidony. Montmorillonite pseudomorphic after shards was found to be relatively rare.

Clinoptilolite pseudomorphs may be either hollow or solid; both types appear somewhat milky or white in reflected light, a fact which aids in recognizing rocks of the clinoptilolite facies with the hand lens. Hollow pseudomorphs consist of a single layer of coarse clinoptilolite crystals with or without a thin marginal layer of finely crystalline clinoptilolite (pl. 2, *b*). The coarse crystals are oriented normal to the walls of the shards, and well-formed crystals terminate in the central cavities. In the solid pseudomorphs, single coarse crystals normal to the walls may extend the full width of the shards, or two opposing layers of crystals may join in the center to form a solid mass of clinoptilolite. Zeolite crystals are randomly oriented in some pseudomorphs. The larger pseudomorphs are more often hollow than are the smaller ones, and hollow pseudomorphs appear to be more common in the montmorillonite subfacies than in the celadonite subfacies. Most of the hollow pseudomorphs have very thin walls within a centimeter of the cavernous zone separating the clinoptilolite facies from the fresh glass facies.

The central cavity in the hollow clinoptilolite pseudomorphs may be partly or wholly filled by calcite, opal, or celadonite. Opal often lines the central cavity uniformly, but sometimes it is present only at the bottom of the central cavity, as if it had formed by the flocculation of colloidal particles, and the upper part of the cavity may be filled by clinoptilolite or calcite (pl. 3, *a*). Opal appears to have been flocculated before any clinoptilolite was formed in some of the composite

opal-zeolite pseudomorphs (pl. 3, *b*). Shards are entirely replaced by opal in local areas of the zeolitized ignimbrite, and they are replaced by calcite in one calcareous concretion which was studied.

This evidence convincingly demonstrates that the clinoptilolite replacements were formed by crystallization of the zeolite within cavities from which the glass had already been dissolved. The arrangement of opal and clinoptilolite in composite pseudomorphs (pl. 3) and the proximity of thin-walled zeolite pseudomorphs to the cavernous zone are difficult to explain in any other way. The pseudomorphic shapes of the cavities were preserved by the preëxisting montmorillonite matrix of the rocks (pl. 2, *a*).

Shards replaced by montmorillonite were found in several of the claystones near the base of the formation, formed by weathering, and in a few zeolite-free claystones formed by diagenetic alteration of ignimbrite. The featureless clay matrix of both tuffs and claystones is probably an alteration product of vitric dust and fine splinters, but there is no evidence either proving or disproving that this vitric material was dissolved before the montmorillonite was formed, as it was in the clinoptilolite pseudomorphs of shards.

Coarse fragments of nonvesicular glass.—Clinoptilolite replacements of fragments of glass 2 mm or more in average diameter in the tuffs and in the unwelded ignimbrite may or may not preserve the welded-tuff texture of the original obsidian. Welded-tuff textures are more common in the coarser fragments than in the smaller ones, and they are almost always preserved in altered chips of obsidian more than a centimeter across. The pseudomorphs in which the original texture is lacking were formed by crystallization of zeolite in cavities from which the glass had already been dissolved; the pseudomorphs preserving the original texture were probably formed by precipitation of zeolite *pari passu* with solution of glass. Both types of pseudomorphic clinoptilolite can almost always be found in the space of a single thin section, and some pseudomorphs are composites of both types.

Clinoptilolite pseudomorphs lacking welded-tuff textures range from thin-walled and hollow to completely solid. They are characteristically colored pinkish-orange by ferric oxide dust included in the margin of the pseudomorphs. Thin curved septa of montmorillonite connect to form a boxwork in most of these pseudomorphs (pl. 4, *a*). Opal and celadonite frequently occur together with the clinoptilolite, and authigenic orthoclase crystals occur locally in the zeolite pseudomorphs 4–8 mm across. The orthoclase seems to be most abundant 15–50 feet above the exposed base of the ignimbrite in center NE $\frac{1}{4}$ sec. 36, T. 10 S., R. 20 E. An outer wall of clinoptilolite, 0.1–0.5 mm thick, typically encloses a porous, spongelike mass of orthoclase euhedra 0.01–0.02 mm in diameter. Orthoclase crystals may form inclusions in the outer wall of clinoptilolite and in single large zeolite crystals extending into the central area.

Formation of pseudomorphs lacking welded-tuff textures can be inferred from obsidian fragments altered to different degrees in the ignimbrite. First, very thin sheets of montmorillonite were formed in the curved fractures in perlitic obsidian. Next, the glass was dissolved, and additional montmorillonite was deposited to thicken the curved sheets, which became connected to form a boxwork whose compartments contained etched relicts of fresh glass until solution was complete. After

the glass was dissolved, zeolite crystallized around the walls of the cavity and over the montmorillonite boxwork.

Pseudomorphs retaining welded-tuff textures may be clinoptilolite alone or they also may contain opal, montmorillonite, or both. Montmorillonite fills narrow curved fractures and forms cores of many of the pseudomorphs 6–10 mm across. Opal may be intergrown with clinoptilolite, or it may be concentrated together with montmorillonite in the core. The zeolite and opal are usually colored pinkish-orange or reddish-brown by included ferric oxide dust; the montmorillonite cores are often brown and waxlike.

Most obsidian fragments more than a centimeter across contain cores of fresh glass which may be directly enclosed by pseudomorphic zeolite 1–5 mm thick, or may be separated from a zeolite margin by a zone of montmorillonite clay 1–5 mm thick which may or may not contain opal. A zone of clay occupies a similar internal position 1–2 mm from the surface of some otherwise fresh obsidian fragments in ignimbrite of the fresh glass facies. This observation implies that the clay zone separating clinoptilolite from fresh glass in zeolitized ignimbrite may have formed before the zeolite, as seems to have been the usual sequence in zeolitic diagenesis, and thus need not necessarily be considered either an intermediate step in replacement of glass by zeolite, or an alteration subsequent to the zeolite.

The welded-tuff texture is preserved in zeolite pseudomorphs by the banding of dust-size grains of ferric oxide that replace the primary magnetite dust of the original obsidian. The welded-tuff texture may be perfectly preserved, or it may be so imperfect as to be almost unrecognizable (pl. 4, *b*). Preservation of the original texture seems compatible with the solution of glass and the precipitation of zeolite, although it does not exclude replacement in the solid state by the diffusion of ions and water molecules through glass. If clinoptilolite had crystallized almost as soon as the glass had been dissolved, the solvent phase between glass and clinoptilolite may have been a mere aqueous interface. If the interface had been narrower than the diameter of the dust-size grains of magnetite in the obsidian (or pseudomorphic ferric oxide), these particles would have remained in place, preserving the original smooth, delicate banding of the iron oxide dust while glass dissolved and zeolite crystallized. Imperfect preservation and distortion of the original texture (pl. 4, *b*) may reflect the settling of iron oxide particles in a solution interface which was at times wider than the diameter of the particles.

Pumice.—The finely tubular, highly porous pumice of claystones is entirely altered to montmorillonite, with or without celadonite; in tuffs, either clay minerals, clinoptilolite, or both of them replace the glass walls, and clay typically fills the vesicles. Glass of the thick-walled, less porous pumice is usually replaced by clinoptilolite, which may form solid or hollow replacements similar to the zeolite pseudomorphs after shards. Vesicles are commonly lined by a thin coating of clay which may either enclose zeolite amygdules or support a layer of clinoptilolite crystals extending into the central cavity. Opal may form a layer between clay and zeolite, or it may fill vesicles lined by clay and zeolite. Globules of opal 0.015 mm across are intergrown with solid clinoptilolite in the vesicles of one pumice fragment examined in thin section. Calcite fills vesicles and replaces glass walls of much pumice in the celadonite subfacies. Most of the calcite fills vesicles lined

by clinoptilolite crystals, but one euhedral crystal of calcite was found to be partly replaced and thinly coated by clinoptilolite. Solid replacements of pumice typify most beds of the celadonite subfacies (pl. 5, *a*), but are relatively rare in the montmorillonite subfacies.

Petrographic relations imply that the clay that lines vesicles in altered pumice was formed before its glass walls were dissolved, and after solution of glass the clay linings in some pumice became connected to form a continuous framework before the clinoptilolite was precipitated. Subsequent crystallization of zeolite locally deformed or disrupted the delicate clay framework (pl. 5, *b*).

ALTERATION OF DEVITRIFIED GLASS

Devitrified shards and pumice of unwelded ignimbrite are locally replaced by montmorillonite, but the amount of montmorillonite that was formed by alteration of already devitrified glass in the ignimbrite is considered small. Shards and chips of devitrified glass are partly replaced by opal in some siliceous concretions in the ignimbrite.

ALTERATION OF PLAGIOCLASE

Orthoclase forms a pseudomorphic replacement of plagioclase in about a third of the 350 thin sections of rocks from the clinoptilolite facies of the John Day Formation, including those from olivine basalt flows and agglomerate. Clinoptilolite (or heulandite) replaces part of a few plagioclase crystals in two samples from the clinoptilolite facies and must be considered a rare occurrence.

Orthoclase may replace part or all of the plagioclase crystals, and rarely it fills fractures in broken plagioclase crystals and forms overgrowths on plagioclase. Most orthoclase replacements retain the shape of the plagioclase crystals, but many pseudomorphs have uneven outlines. Most orthoclase pseudomorphs show uniform sharp extinction, but a few are aggregates of small, irregular crystals. At least some elements of the original plagioclase structure were preserved in orthoclase showing uniform sharp extinction, as (010) is generally common to both plagioclase and the orthoclase which replaces it.

The more calcic plagioclase crystals are replaced selectively, and very little orthoclase was found replacing plagioclase more sodic than An_{20} . The orthoclase replacements occur in all lithologic types of the clinoptilolite facies, but appear to be most common in the dense, zeolite-free claystones in the lower 350 feet of the formation. Higher in the formation they seem to be more common in beds of the celadonite subfacies than in equivalent rocks of the montmorillonite subfacies. Within the olivine basalts, orthoclase is most abundant in scoria and has not been identified in nonvesicular lava. Montmorillonite is a pseudomorphic replacement of plagioclase in some of the highly weathered beds in the lower 100 feet of the formation. Further description of the orthoclase and montmorillonite replacements is given elsewhere (Hay, 1962*a*).

ALTERATION OF PYROXENE

Much of the clinopyroxene (probably augite) having $n_z = 1.710-1.730$ is faintly to highly etched in the montmorillonite subfacies, but appears unaltered or slightly etched in the celadonite subfacies. The ignimbrite and widespread sanidine tuff

contain ferriferous, deep green pleochroic clinopyroxene ($n_z = 1.763 \pm .003$) which is slightly to moderately etched in the celadonite subfacies, but is totally replaced by a golden-colored pleochroic (Z = dark brown, X = pale yellow) phyllosilicate montmorillonoid mineral in both the montmorillonite subfacies and equivalent beds of the fresh glass facies.

Some of the hypersthene (?) crystals in a few tuffs and claystones of the celadonite subfacies are totally replaced by an unidentified phyllosilicate mineral which is brown in reflected light and green in transmitted light. Refractive indices ($n_z = 1.645$, $n_x = 1.615 \pm .005$) are about the same as those of celadonite in these beds. This mineral is assumed to be pseudomorphic after hypersthene, for the associated clinopyroxene is slightly etched or unaltered, and fresh hypersthene is absent in these beds. Etched hypersthene has been noted in single samples from both the celadonite and the montmorillonite subfacies.

CONCRETIONS

Concretions of calcite, opal, and celadonite are present in the clinoptilolite facies of the John Day Formation. Most calcareous concretions are very finely crystalline, but those found in ignimbrite are single large crystals of calcite 3–6 inches across. Zeolite pseudomorphs of shards and pumice fragments are present throughout even the largest concretions in the clinoptilolite facies, suggesting that the calcite was deposited after the zeolite had replaced the glass, for the concretions are relatively impermeable and presumably form a sealed environment. Shards are entirely replaced by calcite in one of the many concretions of the clinoptilolite facies that were examined. Celadonite is invariably less abundant in concretions of the celadonite subfacies than in equivalent nonconcretionary rock, presumably because much of it was replaced by calcite.

Opal of siliceous concretions fills most of the available pore space and may or may not replace vitric and devitrified material. Crystals of heulandite, identified solely on the basis of refractive index, form a coating on opal in the outer, slightly porous part of one concretion found in altered ignimbrite.

The celadonitic concretions, 1–4 cm in diameter, comprise a core of pumice altered to celadonite and clinoptilolite, and an outer mantle, 1–5 mm thick, of tuff matrix densely impregnated with celadonite. The volume ratio of clinoptilolite to celadonite is approximately 2:1 in the central part of the pumice and about 1:1 in the outer 1–2 mm of pumice. The original texture in the pumice is quite distorted (pl. 5, b).

VEINS AND AMYGDULES

Minerals found in veins in the clinoptilolite facies of the John Day Formation are calcite, gypsum, opal, chaledony, clinoptilolite, heulandite, and fluorapatite. Most veins are small, from 1 mm to 1 cm thick. Where clinoptilolite and calcite are present in the same veins, clinoptilolite invariably forms the vein margin and calcite the inner, later deposit. Where clinoptilolite, opal, and chaledony are associated, clinoptilolite forms the vein margin and is succeeded by opal and chaledony, respectively. Heulandite-bearing veins were found only in a thin tuff layer separating two olivine basalt flows in Donnely Basin. In these veins heulandite crystals 1 mm long form the margin and calcite the inner deposit.

Heulandite and calcite were found in vesicles of olivine basalt at several places in Donnelly Basin. Heulandite crystals, 0.1–0.2 mm long, line or fill the vesicles, and calcite fills vesicles lined by heulandite.

PARAGENESIS OF MINERALS

Age relationships can be established for most of the diagenetic minerals of the clinoptilolite facies by the sequence in cavity fillings, by replacement relations, by inclusions of one mineral in another, and by mutual intergrowth of two minerals. In this way it can be shown that opal, orthoclase, and celadonite were locally co-precipitated with clinoptilolite. Nearly all the montmorillonite preceded the clinoptilolite with which it is associated, as much of the celadonite may have done. Calcite was characteristically deposited after the clinoptilolite and heulandite. These conclusions are documented below.

Montmorillonite.—The cavernous zone separating the clinoptilolite facies from the fresh glass facies provides the clearest evidence that montmorillonite was formed diagenetically before clinoptilolite. The clay matrix in most rocks of the fresh glass facies adjacent to the cavernous zone contains only one-half to two-thirds as much montmorillonite as the matrix in the cavernous zone, which preserves molds of shards. This relationship implies that one-third to one-half of the montmorillonite in the cavernous zone was formed or deposited there shortly before the glass shards were dissolved. The clay matrix in rocks of the montmorillonite subfacies resembles that of the cavernous zone; this suggests that little or no matrix montmorillonite was formed after the shards were dissolved in the cavernous zone. A little montmorillonite was found deposited over the surface of the opal that lined a few vesicles in zeolitized pumice.

Celadonite.—Clinoptilolite crystals appear to have grown on the celadonite framework in the pumice of celadonitic concretions (pl. 5, *b*), suggesting that the celadonite was formed before the clinoptilolite. Celadonite locally is intergrown with clinoptilolite crystals pseudomorphic after shards, which indicates that here they crystallized together. The contact of the fresh glass facies and the celadonite subfacies was not found; hence evidence is lacking as to whether the matrix celadonite was formed before solution of the shards, as in most of the montmorillonite in the montmorillonite subfacies, or whether it was formed at a later time.

Opal.—The bulk of opal was precipitated over the same general span of time as the clinoptilolite, judging from the fact that one can be shown to precede the other with about equal frequency, and opal was locally flocculated between two periods of zeolite crystallization (pl. 3, *a*). Local co-precipitation of opal and clinoptilolite is implied by intergrowth of opal and clinoptilolite in some of the pseudomorphs after obsidian fragments, and by globules of opal in clinoptilolite crystals of an amygdale. Heulandite followed opal in the one place where they are associated.

Orthoclase.—Small orthoclase crystals included in coarse clinoptilolite suggest that the two minerals crystallized at the same time. Orthoclase replacements of plagioclase cannot be independently related to the formation of clinoptilolite.

Calcite.—More than 95 per cent of the calcite appears to have been deposited after both the clinoptilolite and the heulandite, judging from mutual relations

in veins and the occurrence of clinoptilolite throughout concretions. Clinoptilolite can be shown to have followed calcite in but a single sample, and nowhere can these minerals be shown to be contemporaneous.

DESCRIPTION OF DIAGENETIC MINERALS

CLINOPTILOLITE AND HEULANDITE

Clinoptilolite and heulandite are closely related forms, the composition and properties of which were recently examined by Mumpton and by Mason and Sand. Mumpton (1960) defines clinoptilolite essentially as Hey and Bannister (1934) did, as the high-silica member of the heulandite structural group; he proposes a range of 5.5–6.5 for the molecular silica/alumina ratio in heulandite and 8.5–10.0 for that in clinoptilolites. Mason and Sand (1960) maintain that the difference lies mainly in the content of lime and alkalis: Ca predominates in heulandites, and Na + K predominate in clinoptilolites. Clinoptilolite has a beta index of 1.485 or lower, and heulandite has a beta index of 1.488 or higher (Mason and Sand, 1960). Heulandite undergoes a reaction to "heulandite B" at about 230°C, whereas clinoptilolite is stable for a period of at least 15 hours at 700°C, according to Mumpton, who suggests an X-ray pattern of material heated overnight at 450°C as a test for distinguishing the two. Both papers maintain that heulandite and clinoptilolite should be considered distinct species having an equal status.

Clinoptilolite is the principal zeolite in the John Day Formation, regardless of which system of classification or criterion is used. The beta index ranges from about 1.476 to $1.485 \pm .002$, and the mineral is stable to at least 600°C, the highest temperature used (table 3). Monovalent cations predominate in both samples which were analyzed (table 4), and the molecular silica/alumina ratios are 8.3 and 8.4, only slightly below the minimum suggested by Mumpton.

Birefringence and refractive indices of most clinoptilolite in the celadonitic subfacies ($n_y = 1.480\text{--}1.485$) are somewhat higher than those of most clinoptilolite in the montmorillonite subfacies ($n_y = 1.476\text{--}1.480$). Substitution of Ca for Na and K in clinoptilolite increases the refractive indices, according to Mason and Sand (1960, p. 350), and their statement is supported by refractive indices and composition of the two clinoptilolites analyzed for the present study. Thus the ratio of Ca to Na + K would seem to be somewhat higher in most clinoptilolite of the celadonite subfacies than in most clinoptilolite of the montmorillonite subfacies.

Heulandite fills cavities in olivine basalt and occurs in veins associated with olivine basalt in the John Day Formation. The beta index ranges from 1.489 to $1.495 \pm .002$, and the material is unstable at temperatures of 300°C (table 3, nos. 4, 5). The molecular silica/alumina ratio is 7.3, which is intermediate between the usual ratios for heulandite and clinoptilolite as recorded by Mumpton (1960). Slightly higher temperatures seem to be required to transform the heulandite of the John Day Formation to "heulandite B" than are necessary for heulandites from Cape Blomidon (Nova Scotia), Paterson (New Jersey), and Mitchell (Oregon) which were studied for comparison (table 3).

TABLE 3
PHYSICAL PROPERTIES OF CLINOPTILOLITE AND HEULANDITE

Name and locality	Cell dimensions and β (1-centered cell)	Optical constants	
		Refractive indices	$2V_z$
1. Clinoptilolite, John Day Formation (table 4, no. 1).	n.d.	n_x n_y between 1.479 and n_z 1.481 \pm .002	n.d.
2. Clinoptilolite, John Day Formation (table 4, no. 2).	$a_o = 15.83 \pm .02\text{\AA}$ $b_o = 17.95 \pm .03\text{\AA}$ $c_o = 7.418 \pm .01\text{\AA}$ $\beta = 91^\circ 45'$	$n_x = 1.481$ -1.483 $n_y = 1.483$ -1.485 $n_z = 1.485$ -1.487	48°-77°
3. Clinoptilolite (?), John Day Formation	$a_o = 15.834 \pm .010\text{\AA}$ $b_o = 17.961 \pm .015\text{\AA}$ $c_o = 7.407 \pm .005\text{\AA}$ $\beta = 91^\circ 42' \pm 5'$	$n_x = 1.484$ $n_y = 1.485$ $n_z = 1.488$	n.d.
4. Heulandite, John Day Formation	n.d.	$n_x = 1.487$ $n_y = 1.489$ $n_z = 1.491$	n.d.
5. Heulandite, John Day Formation (table 4, no. 3)	$a_o = 15.848 \pm .010\text{\AA}$ $b_o = 18.006 \pm .020\text{\AA}$ $c_o = 7.413 \pm .010\text{\AA}$ $\beta = 91^\circ 35'$	$n_x = 1.494^b$ $n_y = 1.495$ $n_z = 1.497$	70°
6. Heulandite, Cape Blomidon, Nova Scotia	n.d.	$n_x = 1.499$ $n_y = 1.501$ $n_z = 1.508$	n.d.
7. Heulandite, Paterson, N. J.	$a_o = 15.86 \pm .01\text{\AA}$ $b_o = 17.92 \pm .02\text{\AA}$ $c_o = 7.424 \pm .01\text{\AA}$ $\beta = 91^\circ 42'$	n.d.	n.d.

^a Phases were identified on basis of diffractometer patterns; three principal d spacings of phases are given below.

Phase A (clinoptilolite and heulandite): 8.9-9.0 \AA (relative intensity = 10), 3.96 \AA (1 = 8), and 2.96 \AA (1 = 6).

Phase B (unidentified): 8.7 \AA (1 = 10), 3.90 \AA (1 = 8), and 2.92 \AA (1 = 6).

Phase C (heulandite B): 8.3 \AA (1 = 10), 5.20 \AA (1 = 4), and 3.63 \AA (1 = 6).

^b Outer margins of many crystals have lower refractive indices; of these, only $n_z = 1.491$ was determined accurately.

Zeolite crystals exhibiting thermal properties of heulandite and refractive indices of clinoptilolite (table 3, no. 3) were found in claystone about 10 feet above the base of the formation near the center W edge sec. 5, T. 11 S., R. 21 E. These properties imply that heulandite and clinoptilolite are not necessarily the separate and distinct species that Mumpton and Mason and Sand considered them to be. The chemical composition of this intermediate zeolite is unknown.

The cell dimensions and angle beta of clinoptilolite and heulandite from the John Day Formation and of heulandite from Paterson, New Jersey, were obtained by Pabst from single-crystal precession patterns (table 3). The measurements on analyzed clinoptilolite of the John Day Formation either fall within the range

Phase(s) present^a and intensity of diffractometer peaks in samples heated 15-20 hours

300°C	400°C	450°C	500°C	600°C
n.d.	n.d.	n.d.	A (strong)	A (strong)
n.d.	n.d.	n.d.	A (strong)	A (strong)
n.d.	A (strong) B (mod.-strong) C (mod.-strong)	A (weak) B (v. weak) C (v. weak)	n.d.	n.d.
n.d.	n.d.	C (mod.)	n.d.	n.d.
A (weak) B (mod.) C (weak-mod.)	C (strong)	C (mod.-strong)	C (barely perceptible)	no pattern
C (strong)	C (weak-mod.)	C (no pattern)	n.d.	n.d.
B (mod.) C (strong)	C (weak-mod.)	C (barely perceptible)	n.d.	n.d.

of variation of heulandite or differ only slightly from heulandite. This information lends no support to the contention that clinoptilolite and heulandite are separate and distinct species.

MONTMORILLONITE

Montmorillonite is used here as a group name and includes all 14Å clay minerals in which the *d* (001) spacing expands to 17-18Å after solvation with glycerol. The montmorillonite of claystones is normal in all respects, but the *d* spacings are unusually weak in diffractometer patterns of the brown clay separating clinoptilolite and fresh glass in the larger fragments of altered obsidian, and from the clay boxwork in cavities from which obsidian had been dissolved. Average refractive indices of the birefringent clay particles from the clay-bearing zones range from 1.535 to 1.570, which is within the range of montmorillonite.

TABLE 4
 CHEMICAL COMPOSITION AND CALCULATED MOLECULAR FORMULA OF CLINOPTILOLITE
 AND HEULANDITE FROM THE JOHN DAY FORMATION

Chemical composition ^a				Composition of unit cell ^b (O = 72)			
Oxides	1	2	3	Constituent	1	2	3
SiO ₂	62.92	64.74	60.37	Atoms per unit cell			
TiO ₂	0.15	0.13	nil	Si.....	28.94	29.25	28.22
Al ₂ O ₃	12.89	13.02	14.05	Al.....	7.00	6.95	7.74
Fe ₂ O ₃	1.60	0.28	tr.	Fe ⁺²	0.07	0.10	0.10
FeO.....	0.18	0.27	0.24	Mg.....	0.17	0.27	0.43
MnO.....	0.01	tr.	tr.	Ca.....	0.84	1.35	3.06
MgO.....	0.25	0.41	0.61	Na.....	2.54	1.53	0.46
CaO.....	1.89	2.79	6.13	K.....	2.53	1.32	0.29
Na ₂ O.....	2.84	1.74	0.51	H ₂ O.....	19.62	21.80	26.86
K ₂ O.....	4.31	2.28	0.48	O.....	72.00	72.00	72.00
P ₂ O ₅	0.07	0.07	0.06	Si/Al.....	4.15	4.21	3.65
CO ₂	0.12	0.12	tr.				
H ₂ O+.....	6.42	12.05	11.43				
H ₂ O-.....	6.32	2.41	5.78				
Total.....	99.97	100.31	99.66				

NOTE: Explanation of column numbers.

1. Clinoptilolite replacing chips of rhyolitic obsidian 2-5 mm across taken from claystone collected 25 feet above exposed base of ignimbrite in center NE $\frac{1}{4}$ sec. 36, T. 10 S., R. 20 E. Feldspar phenocrysts, calcite, and authigenic orthoclase separated from zeolite with heavy liquids; the only impurities noted in analyzed sample are calcite (trace), inclusions of ferric oxide (about 1 per cent), and authigenic orthoclase (about 2 per cent). Sp. gr. of inclusion-free clinoptilolite = 2.13.

2. Clinoptilolite replacing chips of rhyolitic glass 0.5-3 mm across, taken from tuff 165 feet above base of formation in NE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 6, T. 11 S., R. 21 E. Feldspar phenocrysts were separated from zeolite with heavy liquids; only impurity noted is ferric oxide dust, giving zeolite an orange color. Sp. gr. = 2.13-2.17.

3. Heulandite forming margin of a calcite-filled vein 1 cm thick in 12-inch bed of tuff separating two olivine basalt flows along roadcut near center S line SW $\frac{1}{4}$ sec. 29, T. 9 S., R. 23 E. Fine dustlike inclusions of unknown mineral and larger inclusions of a green phyllosilicate mineral are only impurities in analyzed sample, and form less than 0.5 per cent of sample. Sp. gr. of heulandite = 2.19.

^a Analyses made by H. Asari.

^b Fe⁺³, Ti, P, CO₂ (and its equivalent of Ca) were omitted in calculating the unit cell.

CELADONITE

Celadonite is used here to denote an iron-rich, nonexpandable, dioctahedral mica in which potassium is the principal interlayer cation. The (001) spacing is 9.9-10.0Å both in untreated celadonite and in that solvated with glycerol, indicating that the celadonite is free of interstratified montmorillonite. The *d* (060) spacing is 1.505Å, as in dioctahedral micas. The alpha refractive index of celadonite from altered pumice is 1.620 ± .005, and gamma is 1.645 ± .005. One can infer that Fe⁺³ exceeds Al⁺³, Fe⁺² exceeds Mg⁺², and K is the principal interlayer cation in the celadonite by subtracting any probable clinoptilolite composition from a chemically analyzed mixture of celadonite and clinoptilolite (table 7, no. 10).

OPAL

The strongest *d* spacing of alpha cristobalite (4.09Å) and tridymite (4.33Å) can be recognized in all the diffractometer patterns of opal, which closely resemble the patterns of Pliocene opal heated at 900°C for one hour by Franks and Swine-

ford (1959, fig. 4D). The opal may be either isotropic or birefringent; most of the birefringent opal has the granular texture and birefringence of coarsely crystalline chert, but its refractive indices lie between 1.420 and 1.430, which is normal for opal but much too low for chert or chalcedony. The birefringence is unusual for opals but may be due to the tridymite.

ORTHOCLASE

The authigenic orthoclase is a relatively pure monoclinic potash feldspar. Alpha and gamma refractive indices are 1.517 and 1.521 ($\pm .002$), respectively, and $2V_x$ measured with the universal stage is 34° – 39° . Analyzed orthoclase replacements of plagioclase contain less than 1 per cent of the albite molecule in solid solution (Hay, 1962a). The X-ray patterns of both the orthoclase pseudomorphic after plagioclase and the small orthoclase euhedra are those of a single-phase monoclinic potash feldspar containing little or no albite in solid solution. Although optically this feldspar is a member of Tuttle's orthoclase cryptoperthite series (1952), it could be termed adularia on the basis of its low-temperature origin.

ERIONITE (?)

Very small fibers which may be erionite were found attached to clinoptilolite crystals lining the vesicles of a single pumice fragment in ignimbrite of the celadonite subfacies. The fibers exhibit parallel extinction and are length-slow. The alpha refractive index is 1.460 and gamma is 1.464 ($\pm .003$).

MORDENITE (?)

Mordenite (?) fibers of small size were found in the spongelike central areas of some clinoptilolite-orthoclase pseudomorphs after glass chips in ignimbrite of the montmorillonite subfacies at one locality. Extinction is parallel or nearly so, and the fibers are length-fast. Birefringence is low, and refractive indices lie between 1.474 and 1.478.

FLUORAPATITE

Coarsely crystalline fluorapatite forms a few thin veins and fills small cavities; small crystals occur disseminated in claystone and concentrated in grains of altered pumice within the lower 350 feet of the formation. A similar-appearing mineral was noted in pumice fragments of zeolitized ignimbrite. The coarsely crystalline fluorapatite was identified on the basis of X-ray pattern and refractive indices ($n_e = 1.634$).

VERMICULITE

Vermiculite occurs in a number of claystones in the lower 250 feet of beds. It occurs as a replacement of biotite, but also forms elongate, often convolute crystals whose length, parallel to the *c* axis, is at least ten times their width. These vermiform crystals seem to represent an extension of altered biotite. Vermiform crystals are not known to form in the soil profile, so far as the writer is aware, and these crystals are considered diagenetic.

A *d* (002?) spacing of 7.15Å is the only basal spacing observed in unheated vermiculite, but *d* (001) of 10Å was produced by heating the crystal at 700°C

for two hours, thus proving that it is not chlorite or kaolinite. As in vermiculite, the basal spacing does not expand in samples saturated with Mg^{+2} and solvated with glycerol.

KAOLINITE

Coarse vermiform crystals of kaolinite were noted in a few beds of red claystone 100–200 feet above the base of the formation. Their shape suggests that they are diagenetic, perhaps as a result of recrystallization of finely divided kaolinite in these beds. The kaolinite was identified from single-crystal precession patterns.

CHEMICAL CHANGES IN ZEOLITIC DIAGENESIS

CLINOPTILOLITE

Chemical analyses of unaltered obsidian fragments and of clinoptilolite replacing similar obsidian in the same bed show that a gain of water and a loss of silica are the principal changes in replacement of obsidian by clinoptilolite. Alumina has remained constant in the replacement process, for the amount is the same in equal volumes of obsidian and pseudomorphic clinoptilolite, within the analytical limits of accuracy. Change in other chemical components can be determined quantitatively by comparison with alumina (table 5). The gain of Ca and Mg and the loss of Na, K, and Fe are small in comparison with the change in SiO_2 and H_2O but large in terms of the amounts originally present in the obsidian. Similar changes may have taken place in the formation of the other sample of analyzed clinoptilolite (table 4, no. 2) from rhyolitic glass, judging from the fact that the ratio of Si to Al and of Na + K to C and the amount of Fe are lower than normal for rhyolites. Gains of Ca and corresponding losses of alkalis are suggested by

TABLE 5
CHEMICAL CHANGES IN FORMATION OF CLINOPTILOLITE FROM RHYOLITIC OBSIDIAN

Ion	Obsidian ^a (Barth standard cell)	Clinoptilolite ^b	Losses		Gains	
			Ions/std. cell	Per cent	Ions/std. cell	Per cent
Si.....	60.4	47.8	12.6	21
Ti.....	0.2	0.2
Al.....	11.6	11.6
Fe.....	1.9	1.0	0.9	47
Fe ⁺³	0.7	0.9	0.2	29
Fe ⁺²	1.2	0.1	1.1	92
Mn.....	0.1	0.0	0.1	100
Mg.....	0.2	0.3	0.1	50
Ca.....	0.7	1.6	0.9	130
Na.....	5.1	4.2	0.9	18
K.....	5.2	4.2	1.0	19
P.....	0.1	0.1
H (as H ₂ O).....	12.8	32.4	19.6	153
C (as CO ₂).....	0.0	0.1	0.1	> 100
O.....	160.0	152.0	8.0	5

^a Composition of standard cell calculated from table 7, no. 1.

^b Composition calculated from table 4, no. 1, assuming amount of alumina to be same as in obsidian.

refractive indices of most clinoptilolite replacing rhyolitic glass in the ignimbrite of the celadonite subfacies (see p. 233). Since some or all of the Ca, Na, and K ions occupy exchangeable cation sites in the clinoptilolite structure, their proportions may have been modified at any time after the zeolite was formed.

ANALYZED BULK SAMPLES

Altered vitric rhyolitic rocks of the clinoptilolite facies fall into two groups representing roughly equal thicknesses of beds when the bulk chemical analyses (table

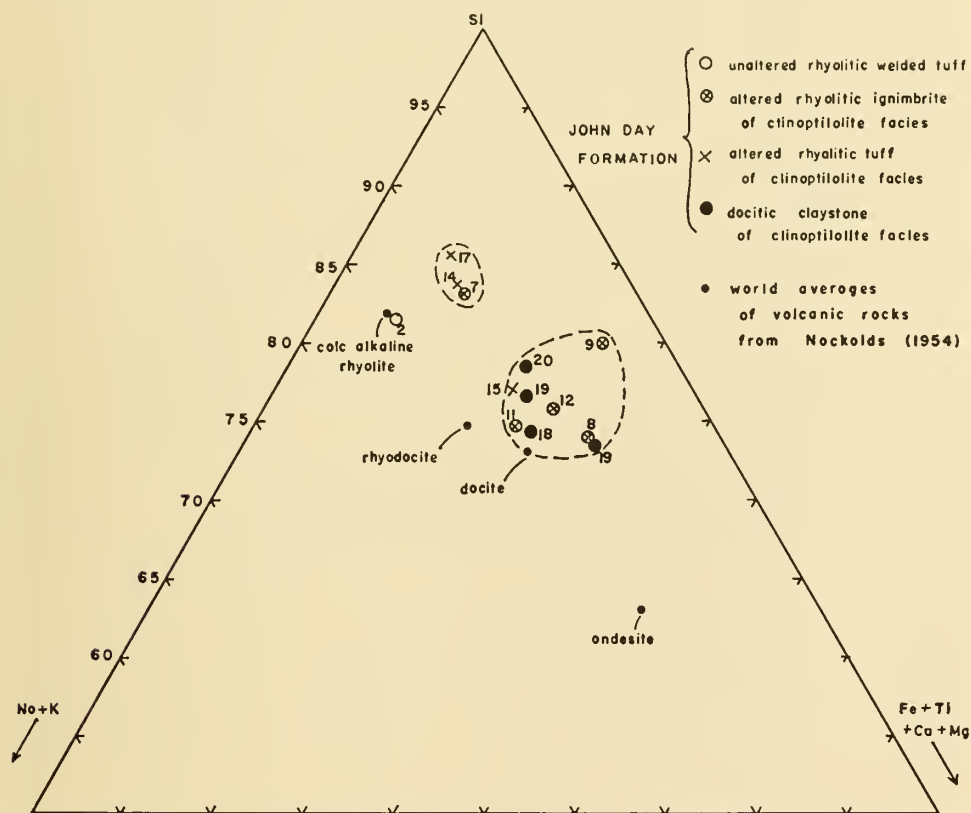


Fig. 9. Rocks of the John Day Formation and world averages taken from Nockolds (1954) are plotted in terms of molecular percentage of Si, Na + K, and Fe + Ti + Mg + Ca. The calcium represented by calcite is excluded from the diagram. Numbers represent analyses of table 7.

7) are plotted in terms of Si, Fe + Ti + Mg + Ca, and Na + K (fig. 9). Claystones formed by alteration of dacitic glass are chemically similar to the group of rocks richest in Fe + Ti + Mg + Ca, and the following evidence is intended to show that the similarity has resulted from the exchange of ions by vitric rhyolitic and dacitic beds during diagenesis. Most of the devitrified ignimbrite has been modified to a small extent, if at all, by diagenetic processes.

Altered vitric ignimbrite.—Chemical changes can be rather reliably inferred for the zeolitized ignimbrite by comparing analyses of fresh and altered ignimbrite and assuming that the amount of alumina has remained unchanged. Slight

TABLE 6
CHEMICAL CHANGES IN ZEOLITIC DIAGENESIS OF RHYOLITIC IGIMBRITE^a

Ion	Montmorillonite subfacies						Celadonite subfacies		
	1	2	3	4	5	6	7	8	
Si.....	59.3	65.8 (+6.5)	59.6 (+0.3)	52.4 (-6.9)	34.1 (-25.2)	57.6 (-1.7)	48.2 (-11.1)	50.9 (-8.4)	
Ti.....	0.2	0.2	0.3 (+0.1)	0.9 (+0.7)	0.2	0.5 (+0.3)	0.7 (+0.5)	0.7 (+0.5)	
Al.....	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7	
Fe.....	1.9	1.8 (-0.1)	2.3 (+0.4)	6.2 (+4.3)	2.7 (+0.8)	7.9 (+6.0)	5.0 (+3.1)	5.1 (+3.2)	
Fe ⁺³	0.7	1.6 (+0.9)	2.3 (+1.6)	6.2 (+5.5)	2.7 (+2.0)	5.4 (+4.7)	4.3 (+3.6)	4.3 (+3.6)	
Fe ⁺²	1.2	0.2 (-1.0)	tr.	0.0 (-1.2)	0.0 (-1.2)	2.5 (+1.3)	0.7 (-0.5)	0.8 (-0.4)	
Mn.....	0.1	0.0 (-0.1)	0.0 (-0.1)	0.1	0.0 (-0.1)	0.1	0.1	0.1	
Mg.....	0.3	0.6 (+0.3)	0.4 (+0.1)	2.8 (+2.5)	2.5 (+2.2)	2.0 (+1.7)	1.4 (+1.1)	1.8 (+1.5)	
Ca.....	0.8	2.9 (+2.1)	1.4 (+0.6)	3.3 (+2.5)	1.6 (+0.8)	4.1 (+3.3)	2.1 (+1.3)	4.9 (+4.1)	
Na.....	5.8	4.7 (-1.1)	1.8 (-4.0)	3.1 (-2.7)	1.2 (-4.6)	3.5 (-2.3)	3.5 (-2.3)	2.1 (-3.7)	
K.....	4.2	3.5 (-0.7)	5.0 (+0.8)	2.0 (-2.2)	0.3 (-3.9)	6.4 (+2.2)	3.5 (-0.7)	3.3 (-0.9)	
P.....	0.1	0.6 (+0.5)	0.2 (+0.1)	0.3 (+0.2)	0.1	0.9 (+0.8)	0.2 (+0.1)	0.2 (+0.1)	
H (as H ₂ O).....	13.0	48.1 (+35.1)	37.9 (+24.9)	46.3 (+33.3)	44.7 (+31.7)	40.5 (+27.5)	35.5 (+22.5)	40.5 (+27.5)	
C (as CO ₂).....	0.0	0.2 (+0.2)	0.0	0.4 (+0.4)	0.0	0.7 (+0.7)	0.1 (+0.1)	2.0 (+2.0)	
O.....	160.0	210.5 (+50.5)	178.6 (+18.6)	187.2 (+27.2)	139.7 (-20.3)	199.6 (+39.6)	165.9 (+5.9)	182.5 (+22.5)	

Note: Explanation of column numbers.

- Densely welded vitric tuff (table 7, no. 2).
 - Altered fragment of pumice from montmorillonite subfacies (table 7, no. 6).
 - Zeolitized ignimbrite of montmorillonite subfacies (table 7, no. 7).
 - Zeolite claystone of montmorillonite subfacies (table 7, no. 8).
 - Zeolite-free claystone of montmorillonite subfacies (table 7, no. 9).
 - Altered fragments of pumice from celadonite subfacies (table 7, no. 10).
 - Zeolitized ignimbrite of celadonite subfacies (table 7, no. 11).
 - Zeolitized ignimbrite of celadonite subfacies (table 7, no. 12).
- ^a Calculations assume that all the ignimbrite originally had the composition of analysis 1, and alumina remained constant in alteration. Change is indicated as ions or water molecules gained (+) or lost (-) per Barth standard cell of original rhyolitic ignimbrite.

changes in the content of alumina cannot be denied, but the assumption of constant alumina seems to be at least approximately correct, for changes in the content of oxygen atoms calculated on this basis (table 6) agree with the volume changes estimated from thin sections. If any other major element or ion (e.g., Si or Fe^{+3}) is assumed to be constant, the calculated changes in oxygen content contradict petrographic evidence concerning the volume change. Constant alumina is also consistent with the nature of the principal chemical reactions: the amount of alumina remains unchanged in replacement of rhyolitic glass by clinoptilolite, and alumina may remain fixed in the leaching of glass to form montmorillonite.

In zeolitized ignimbrite of the montmorillonite subfacies the amount of silica has remained almost constant (table 6, no. 3), and the silica which was released in forming clinoptilolite from glass is probably represented by opal. This one analyzed sample, which contains authigenic orthoclase, appears to have gained a small amount of potassium. Claystones formed by alteration of ignimbrite (table 6, nos. 4, 5) have lost a considerable amount of silica and have gained much more Fe, Ti, Mg, and Ca than has the zeolitized ignimbrite of the montmorillonite subfacies (table 6, no. 3). Zeolitized ignimbrite of the celadonite subfacies is chemically similar to claystones of the montmorillonite subfacies except for a higher $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio.

Large fragments of altered pumice in rhyolitic ignimbrite differ in their chemical change from the rock containing the pumice fragments. A large pumice fragment of zeolitized pumice from the montmorillonite subfacies (table 6, no. 2) gained noteworthy amounts of Si, P, and O, unlike the bulk sample of zeolitized ignimbrite from the same locality (table 6, no. 3). The gain of silica is represented by opal, which replaces glass and fills vesicles, and apatite amygdules may account for the fivefold increase in P. Pumice from cores of celadonitic concretions (table 6, no. 6) shows the greatest enrichment in total Fe, Fe^{+2} , K, and P found in altered rhyolitic rocks of the John Day Formation. This analysis is easy to interpret mineralogically, for the pumice fragments are now about 99 per cent celadonite and clinoptilolite. The Fe, Ti, Mg, and P must be contained mostly in the celadonite, as these ions normally do not occur in more than trace amounts in clinoptilolite. Calcium is contained in the clinoptilolite, since it does not normally occur in celadonite, and this inference is supported by the relatively high refractive indices of most clinoptilolite in this pumice ($n_z = 1.488 \pm .002$).

Altered vitric rhyolitic tuff.—Two samples of zeolitized rhyolitic tuff of the montmorillonite subfacies (table 7, nos. 14, 16) chemically resemble the zeolitized ignimbrite of the same subfacies (table 7, no. 7), and one sample of celadonitic zeolitized rhyolite tuff is chemically similar to zeolitized ignimbrite of the celadonite subfacies. These similarities suggest that the same chemical changes have occurred in alteration of both tuff and ignimbrite within each subfacies. A sample of vitric rhyolite tuff with fresh glass (table 7, no. 13) is chemically similar to zeolitized tuff from the same stratigraphic unit at another locality (table 7, no. 14). Their close similarity seems to suggest that here there was little chemical change in zeolitic alteration, but the two analyses are not adequate proof of this possibility.

TABLE 7
CHEMICAL ANALYSES OF ROCKS FROM THE JOHN DAY FORMATION

Oxides	1	2	3	4	5	6	7	8	9
SiO ₂	71.36	70.85	73.56	75.20	70.98	64.32	66.05	55.36	52.11
Al ₂ O ₃	11.57	11.90	12.78	12.49	13.37	9.67	11.00	10.45	15.07
Fe ₂ O ₃	1.06	1.12	2.07	0.33	2.28	2.10	3.42	8.71	5.43
FeO	1.74	1.69	0.09	nil	0.11	0.21	tr.	tr.	tr.
MgO	0.17	0.27	0.24	0.06	0.12	0.36	0.70	1.96	2.52
CaO	0.71	0.91	0.66	0.66	0.35	2.66	1.46	3.23	2.24
Na ₂ O	3.09	3.61	3.89	2.73	4.24	2.35	1.29	1.69	0.92
K ₂ O	4.85	3.99	3.86	5.93	3.17	2.69	4.37	1.64	0.39
TiO ₂	0.30	0.30	0.38	0.44	0.25	0.83	0.42	1.18	0.40
MnO	0.05	0.05	tr.	tr.	0.01	0.02	0.02	0.13	0.09
P ₂ O ₅	0.07	0.10	0.10	0.14	0.04	0.71	0.28	0.38	0.11
H ₂ O (-)	0.68	1.27	0.97	0.64	1.82	7.20	5.82	9.03	15.18
H ₂ O (+)	3.84	3.44	1.00	0.88	2.62	6.87	5.10	5.64	5.24
CO ₂	n.d.	n.d.	0.05	0.03	n.d.	0.11	nil	0.30	tr.
SO ₄ ⁻²	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	99.49	99.50	99.65	99.53	99.36	100.10	99.93	99.70	99.70

NOTE: Explanation of column numbers.

1. Glass ($n = 1.506 \pm .002$) from 2-3 cm fragments of black densely welded vitric tuff collected from basal 25-foot-thick flow unit of ignimbrite in center N $\frac{1}{2}$ SW $\frac{1}{4}$ sec. 31, T. 10 S., R. 21 E. Phenocrysts were separated from glass with heavy liquids. Sp. gr. of glass = 2.38. H. Asari, analyst.

2. Pale gray densely welded vitric tuff collected 7 feet above base of ignimbrite, near SW cor. sec. 1, T. 10 S., R. 22 E. In point-counted thin section, glass ($n = 1.504 \pm .002$) forms 97.7 per cent of rock (by vol.); plagioclase (principally An₁₂), 1.1 per cent; rock fragments, 1.4 per cent; iron-rich clinopyroxene ($n_x = 1.762 \pm .003$), 0.1 per cent. Sp. gr. of rock = 2.37. H. Asari, analyst.

3. Yellowish-gray devitrified densely welded tuff collected 6 feet above base of a 40-foot unit of welded tuff in NW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 31, T. 10 S., R. 21 E. Glass has devitrified to alkali feldspar and alpha cristobalite, which now form 97.7 per cent (by vol.) of a point-counted thin section; pyroxene (altered to a green phyllosilicate mineral), 1.1 per cent; plagioclase (An₁₂), 0.7 per cent; rock fragments, 0.5 per cent. Sp. gr. of rock = 2.50. H. Asari, analyst.

4. Very light gray moderately porous semiwelded devitrified tuff collected 3 feet above base of a 15-foot unit of devitrified tuff forming a hogback in NW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 36, T. 10 S., R. 20 E. Glass has devitrified to alpha cristobalite and alkali feldspar, which are estimated to form 98 per cent (by vol.) of a thin section; plagioclase phenocrysts (An₁₂), 1 per cent; rock fragments, 1 per cent; altered pyroxene, a trace. Relatively pure potash feldspar (mean refractive index = 1.520) is dominant alkali feldspar of devitrified glass. H. Asari, analyst.

5. Fragments of pale yellowish-brown devitrified glass 2-8 mm in diameter collected 5-10 feet above base of claystone overlying a 40-foot thickness of massive devitrified welded tuff in center S line NW $\frac{1}{4}$ sec. 31, T. 10 S., R. 21 E. Glass has devitrified to alkali feldspar and alpha cristobalite, which are estimated to form 99 per cent (by vol.); plagioclase (An₁₂), about 1 per cent; altered pyroxene, a trace. H. Asari, analyst.

6. Yellowish-gray thick-walled zeolitized pumice fragment of montmorillonite subfacies collected 25-30 feet above exposed base of ignimbrite in center NE $\frac{1}{4}$ sec. 36, T. 10 S., R. 20 E. Volume of pumice fragment about 2 cubic inches. In thin section clinoptilolite is estimated to form 84 per cent (by vol.) of pumice and vesicle fillings; montmorillonite, 8 per cent; opal, 7 per cent; plagioclase (An₁₂), 1 per cent; apatite (?) amygdules, a trace. H. Asari, analyst.

7. Grayish-yellow zeolitized ignimbrite of montmorillonite subfacies, collected 15 feet above exposed base of ignimbrite at same locality as no. 6. In thin section clinoptilolite is estimated to form 60 per cent (by vol.); montmorillonite, 37 per cent; plagioclase (An₁₂), 1 per cent; rock fragments, 1 per cent; opal, 1 per cent; opaque ores and authigenic orthoclase, a trace. H. Asari, analyst.

8. Dusky yellow zeolitic claystone of montmorillonite subfacies, collected from ignimbrite about 35 feet below a layer of welded tuff in center SW $\frac{1}{4}$ sec. 33, T. 10 S., R. 21 E. In thin section clinoptilolite is estimated to form 30 per cent (by vol.); montmorillonite, 66 per cent; plagioclase (An₁₂), 2 per cent; rock fragments, 1 per cent; opal, 1 per cent; pyroxene and calcite, a trace. H. Asari, analyst.

9. Dusky yellow zeolite-free claystone of montmorillonite subfacies collected from 5 feet of altered ignimbrite underlying devitrified welded tuff in center N $\frac{1}{2}$ SW $\frac{1}{4}$ sec. 31, T. 10 S., R. 21 E. In a disaggregated sample, montmorillonite forms 94.5 per cent (by wt.); plagioclase (An₁₂), rock fragments, and spherulites of alkali feldspar and alpha cristobalite total 5.5 per cent. H. Asari, analyst.

10	11	12	13	14	15	16	17	18	19	20
55.25	57.18	55.61	66.35	66.49	60.92	71.67	49.86	50.19	52.83	50.77
9.47	11.72	10.82	12.12	11.78	12.52	11.58	16.09	18.41	13.52	12.29
6.89	6.85	6.23	3.12	2.67	3.92	1.46	6.53	5.67	9.05	8.71
2.83	0.98	0.97	0.62	0.26	1.55	0.28	nil	nil	nil	nil
1.30	1.13	1.35	0.85	0.61	1.24	0.44	0.83	1.20	1.57	1.90
3.63	2.32	4.97	1.37	1.77	3.37	2.01	2.71	2.91	3.24	3.67
1.75	2.16	1.25	1.70	2.11	2.30	1.67	1.34	2.81	1.56	1.82
4.79	3.28	2.78	3.67	2.80	2.64	3.38	3.26	0.48	1.58	1.48
0.63	1.14	1.05	0.45	0.54	0.82	0.57	1.74	1.12	1.10	1.25
0.10	0.13	0.13	0.04	0.02	0.07	0.05	0.08	0.05	0.07	0.08
1.05	0.26	0.29	0.08	0.10	0.20	0.01	0.09	0.05	0.43	0.69
4.67	5.99	6.29	3.92	4.62	4.51	3.39	11.48	11.92	10.50	12.31
6.93	6.62	6.97	5.56	5.81	5.99	3.51	6.14	5.33	4.37	5.29
0.49	0.05	1.59	tr.	tr.	0.11	nil	nil	nil	tr.	0.04
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.19	0.06	0.04	n.d.	n.d.
99.78	99.81	100.24	99.85	99.58	100.16	100.21	100.21	100.18	99.82	100.30

10. Grayish-green fragments of altered pumice 1-2 cm long from centers of celadonic concretions from celadonite subfacies collected 30-50 feet above base of ignimbrite in center S edge NW $\frac{1}{4}$ sec. 22, T. 10 S., R. 22 E. Clinoptilolite is estimated to form 60 per cent (by vol.); celadonite, 39 per cent; plagioclase (An₁₂), 1 per cent of pumice (see pl. 5, b). H. Asari, analyst.

11. Dusky yellowish-green zeolitized ignimbrite of celadonite subfacies collected from same location as no. 10. Clinoptilolite is estimated to form 50 per cent (by vol.); celadonite and montmorillonite, 45 per cent; plagioclase (An₁₂), 2 per cent; rock fragments, 3 per cent; calcite, a trace. H. Asari, analyst.

12. Dusky yellowish-green zeolitized ignimbrite of celadonite subfacies collected 90-100 feet above base of ignimbrite in center S $\frac{1}{2}$ SW $\frac{1}{4}$ sec. 1, T. 10 S., R. 22 E. Clinoptilolite is estimated to form 45 per cent (by vol.); celadonite and montmorillonite, 43 per cent; calcite, 9 per cent; rock fragments, 2 per cent; plagioclase (An₁₂), 1 per cent. H. Asari, analyst.

13. Yellowish-gray coarse vitric tuff of fresh glass facies collected from 65-foot unit of medium- to coarse-grained tuff about 200 feet below ignimbrite in NE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 13, T. 10 S., R. 20 E. Glass is estimated to form 60 per cent (by vol.); montmorillonite, 36 per cent; feldspar (sanidine with minor labradorite), 3 per cent; rock fragments, 1 per cent. H. Asari, analyst.

14. Composite of two yellowish-gray zeolitized tuff samples of montmorillonite subfacies collected from 45-foot unit of medium- to coarse-grained tuff about 215 feet below ignimbrite in NW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 31, T. 10 S., R. 21 E. Clinoptilolite is estimated to average 56 per cent (by vol.); montmorillonite, 38 per cent; feldspar (sanidine and An₄₂₋₅₄ plagioclase about equal), 4 per cent; rock fragments, 2 per cent; opal, a trace. H. Asari, analyst.

15. Composite of two grayish-green zeolitized tuff samples of celadonite subfacies collected from medium- and coarse-grained tuff 150-170 feet below ignimbrite in center S $\frac{1}{2}$ SW $\frac{1}{4}$ sec. 22, T. 10 S., R. 22 E. Clinoptilolite is estimated to average 53 per cent (by vol.); celadonite and montmorillonite, 40 per cent; feldspar (An₃₆₋₅₄ plagioclase with lesser sanidine), 4 per cent; rock fragments, 3 per cent; calcite, a trace. H. Asari, analyst.

16. White fine-grained zeolitized tuff of montmorillonite subfacies collected about 170 feet above base of formation in center N edge NE $\frac{1}{4}$ sec. 1, T. 11 S., R. 20 E. In point-counted thin section coarsely crystalline clinoptilolite forms 6.8 per cent (by vol.); plagioclase, sanidine, and authigenic orthoclase, 2.1 per cent; rock fragments, 4.4 per cent; remaining 86.7 per cent is a mixture of finely crystalline clinoptilolite, opal, and montmorillonite. W. H. Herdsman, analyst.

17. Dusky yellow claystone of montmorillonite subfacies collected 65 feet above base of formation near SW cor. sec. 36, T. 10 S., R. 20 E. In point-counted thin section montmorillonite forms 83.9 per cent (by vol.); orthoclase replacement of plagioclase crystals, 5.7 per cent; rock fragments (most contain plagioclase replaced by orthoclase), 4.8 per cent; quartz, 0.6 per cent. Orthoclase totals about 8 per cent of rock. W. H. Herdsman, analyst.

18. Pale yellowish-green claystone of montmorillonite subfacies collected approximately 250 feet above base of formation at E edge NE $\frac{1}{4}$ sec. 1, T. 11 S., R. 20 E. Montmorillonite forms 91.8 per cent (by wt.) of disaggregated sample; plagioclase (An₄₀₋₄₆), 6.6 per cent, sand-size rock fragments, 1.6 per cent. W. H. Herdsman, analyst.

19. Dusky yellow claystone of montmorillonite subfacies collected 165 feet below ignimbrite in NW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 31, T. 10 S., R. 21 E. Montmorillonite is estimated to form 89 per cent (by vol.); plagioclase (principally An₁₂), 5 per cent; rock fragments, 5 per cent; calcite, 1 per cent. H. Asari, analyst.

20. Dusky yellow claystone of montmorillonite subfacies collected 80 feet above ignimbrite near NW cor. sec. 36, T. 10 S., R. 20 E. Montmorillonite is estimated to form 92 per cent (by vol.); plagioclase (An₄₆₋₅₂), 3 per cent; rock fragments, 5 per cent. H. Asari, analyst.

Altered vitric dacitic pyroclastic deposits.—Four analyses of dacitic claystone are given in table 7 (nos. 17–20), but diagenetic chemical changes can be demonstrated only in the one claystone which contains 8 per cent of authigenic orthoclase (table 7, no. 17). This claystone was formed by weathering of vitric ash at the land surface, where it should have been leached of most of its original potassium, yet it now contains 3.8 per cent K_2O , on a water-free basis. This percentage of K_2O is more than one would expect to find in unweathered dacite glass, and must represent some addition. Silica must also have been introduced into this bed, as the orthoclase replaces andesine. The authigenic orthoclase in many other claystones in the lower 350 feet of the formation (Hay, 1962a) suggests widespread enrichment in K and Si. Additional Si may have been gained by dacitic rocks containing clinoptilolite, for the ratio of Si to Al in most dacite is lower than in clinoptilolite.

Altered devitrified ignimbrite.—The devitrified densely welded tuff (table 7, no. 3) is chemically similar to vitric welded tuff (no. 2), whereas the devitrified semiwelded tuff (no. 4) and small chips of devitrified glass (no. 5) differ in several respects from the vitric tuff (see also table 1). All these rocks, however, contain similar plagioclase phenocrysts (An_{12}), which would not be expected if they had crystallized from magmas differing as widely as the five analyzed samples. Hence it is likely that some or all of these rocks were modified after the ignimbrite was emplaced. The devitrified semiwelded tuff and chips of devitrified glass depart rather widely from the other three samples, and they differ from each other, suggesting that they have been modified more extensively than the others, which may be essentially unchanged except possibly for hydration (table 7, nos. 1, 2) and oxidation and possibly dehydration (no. 3).

The devitrified semiwelded tuff and glass chips could have been chemically modified by hot gases streaming through the porous ignimbrite soon after its emplacement, or, at a much later time, by subsurface water. A few plagioclase crystals in devitrified ignimbrite interbedded within the clinoptilolite facies are partly or wholly replaced by orthoclase, as they often are in tuffs and claystones of the clinoptilolite facies; this suggests that a small amount of potassium has been added to or redistributed within the devitrified ignimbrite during zeolitic diagenesis. Unfortunately there seems to be no direct way of proving whether the total change in chemical composition should also be attributed to diagenesis.

SUMMARY OF CHEMICAL CHANGES

The replacement of rhyolitic glass by clinoptilolite involved a gain of H_2O , Ca, and Mg, and a loss of Si, Na, K, and Fe. Altered vitric rocks of original rhyolitic composition gained Fe, Ti, Mg, Ca, and less commonly P. Some of the alkalis were lost; silica was lost from about half of the altered rhyolitic rocks, but remained nearly constant in the others. About half of the altered rhyolitic rocks now resemble the altered dacitic rocks in chemical composition (fig. 9 and table 7), and their close chemical similarity strongly argues that ions were extensively exchanged by rhyolitic and dacitic beds: the K and Si lost by the rhyolitic deposits were gained by the dacitic beds, and the Fe, Ti, Mg, Ca, and P gained by the rhyolitic rocks were supplied by the dacitic beds.

Most ions in the clinoptilolite facies occupy sites within silicate structures where they must have become fixed at the time the montmorillonite, clinoptilolite, celadonite, opal, and orthoclase were formed. Later chemical changes must have been limited mostly to addition of Ca as calcite and possibly to changes in the proportions of Na, K, Ca, and Mg in the sites of exchangeable cations in montmorillonite and clinoptilolite.

The ratio of Na to K was locally changed within the devitrified ignimbrite after its eruption, but primary hot gases rather than cold subsurface water may have redistributed the alkalis.

MECHANISM OF ZEOLITIC DIAGENESIS

TEMPERATURE AND PRESSURE

The temperature of zeolitic diagenesis was determined by the local geothermal gradient and burial depth, for a hydrothermal origin can be eliminated, and a few thin dikes are the only local sources of heat known to exist. The broad areal extent and roughly horizontal surface of the clinoptilolite facies are the most convincing arguments against hydrothermal solutions. Most or all zeolitic diagenesis occurred at depths between 1,250 and 4,000 feet, which represent temperatures of 27.5° and 55°C, assuming an average gradient of 1°C per 100 feet and an average surface temperature of 15°C. Hydrostatic pressures at these depths should have been 35–120 atm., assuming that the water table lay within 100 feet of the surface. The rise in temperature and pressure with depth in the John Day Formation seems too slight to account for the restriction of the clinoptilolite facies to the lower half of the formation.

WATER COMPOSITION

The different diagenetic facies and subfacies must reflect differences in the composition of subsurface water. Clinoptilolite, orthoclase, and celadonite were probably formed where the water was more alkaline and saline than that which permeated the beds in which only montmorillonite was formed. Subsurface water in dacitic beds of the clinoptilolite facies did not generally differ from that in rhyolitic beds, but the Eh varied laterally within both types of beds. Water saturating the olivine basalts of Donnelly Basin probably had a lower ratio of Na + K to Ca and possibly of Si to Al than that permeating the silicic pyroclastic deposits. These conclusions are based on the following considerations.

1. Clinoptilolite probably required relatively high activity ratios of Si to Al, and of Na + K to H. Clinoptilolite has the highest Si/Al ratio of the zeolites commonly formed by low-temperature zeolitic diagenesis, which include analcite, erionite, phillipsite, and heulandite. Co-precipitation of opal and clinoptilolite proves that the zeolite locally crystallized from a solution supersaturated with respect to quartz, tridymite, and cristobalite. Absolute values for the activity ratio of Na + K to H required to form clinoptilolite cannot be inferred from the published literature, but a higher ratio of Na + K to H should have been required to form clinoptilolite than to form montmorillonite. In the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, Hemley (1961) found that analcite-montmorillonite equilibria are a

function of the activity ratio of Na to H, with analcite forming at the higher values. Presumably the same relations prevail in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, where montmorillonite and clinoptilolite are formed alternatively, as in the John Day Formation.

2. Experiments at room temperature by Garrels and Howard (1959) indicate that potash feldspar should be stable at 25°C only in solutions having a K-ion to H-ion activity ratio of at least 10^{9-10} , which represents a K-ion activity of 1-10N at a pH of 9. Hemley (1959), working between 200° and 500°C , achieved results which extrapolate to room temperature in agreement with those of Garrels and Howard. The ratio of K to H in the John Day Formation may have been considerably lower than 10^9 , notwithstanding the results of laboratory experiments. Orthoclase replaces plagioclase, according to Mellis (1960), in the outer part of gabbro fragments from a short core taken from the deep-sea floor. The replacement relationships are similar to those in the John Day Formation, and the shallow depth (about 2 inches) at which some of them occur suggests that the interstitial water was not greatly different from sea water, in which the ratio of K to H is $10^{5.5-6}$. These orthoclase replacements of plagioclase may, however, have formed far outside their true stability field because of nucleation by the plagioclase being replaced. The small orthoclase euhedra which crystallized in the altered ignimbrite show no evidence of nucleation by preexisting crystals and may have required conditions more nearly approaching those suggested by the laboratory experiments.

3. The composition of water saturating the dacitic beds at the time of zeolitic diagenesis must have been about the same as that in the rhyolitic beds, for the same diagenetic minerals occur in the two types of beds. If, for example, the activity ratios of Si to Al and of Na + K to Ca had been significantly lower in water in the dacitic beds than in the rhyolitic beds, different zeolite species might reasonably be expected, such as heulandite or analcite in the dacitic beds and clinoptilolite in the rhyolitic beds. The occurrence of heulandite rather than clinoptilolite in the olivine basalts does suggest, however, that activity ratios of Si to Al or of Na + K to Ca were lower in solutions permeating the basalts than in those of the silicic pyroclastic beds.

4. The Eh of the water varied in different areas within the pyroclastic deposits. Celadonite required a higher activity of Fe^{+2} (hence a lower Eh) than prevailed where only montmorillonite was formed: the celadonite contains ferrous iron (table 7, no. 10), whereas the montmorillonite usually contains only ferric iron. Bulk samples of all analyzed rocks from the celadonite subfacies contain at least 0.97 per cent FeO; rocks of the montmorillonite subfacies never contain more than 0.28 per cent FeO.

Highly alterable clinopyroxene rich in Fe^{+2} has been preserved in beds of the celadonite subfacies, but it was altered to a golden-colored montmorillonite probably containing Fe^{+3} in beds of the montmorillonite subfacies. This fact can be attributed to the lower Eh in water of the celadonite subfacies.

CLIMATE AND DEPTH OF THE WATER TABLE

Saline, alkaline lake water need not be considered as a source of subsurface water, for this would require an arid climate incompatible with the mid-Tertiary climate in this area. Floras collected from the Upper Oligocene part of the John Day Formation and from the transitional Middle-Upper Miocene Mascall formation are most similar to present-day floras receiving 50 inches of rainfall per year (Chaney, 1952, p. 108; 1959, p. 59). Furthermore, a recent evaluation of 48 well-documented Tertiary floras of the western United States (Wolfe and Barghoorn, 1960) shows that the floral change through the Tertiary was gradual, which is incompatible with the idea of a semiarid or arid climate during Early and Middle Miocene time.

The water table marks a sharp change in the subsurface environment, which might seem to account for the position of the clinoptilolite facies below the fresh glass facies, and for the sharp separation of the two facies. Several facts argue against this explanation, however. The depth of 1,000–1,250 feet to the top of the clinoptilolite facies in the area represented by figure 3 seems much too great for the permanent water table in an area where the rocks were of low permeability and the rainfall 30 inches or more per year. The depth to the clinoptilolite facies may have originally been much greater than 1,250 feet, for an unknown amount was eroded from the top of the formation before the Columbia River Basalt was deposited.

ORIGIN BY LEACHING IN AN OPEN SYSTEM

The leaching experiment of Morey and Fournier (1961) seems to provide a model which can account for the restriction of the clinoptilolite facies to the lower part of the John Day Formation. Morey and Fournier slowly pumped pure water down through a column of finely ground nepheline at 295°C and 2,500 p.s.i. When the experiment was terminated, boehmite and paragonite had replaced all the nepheline at the top of the sample container, where only fresh water came in contact with the sample. Muscovite and analcite had been formed at the exit end of the container, where the water had attained an average pH of 9.7 and an ion concentration of 440 p.p.m. The boehmite and paragonite represent the products of leaching where the activity ratio of alkali ions to hydrogen ions was low; solution and hydrolysis of the nepheline progressively raised the pH and ion concentrations to levels at which muscovite and analcite crystallized. By comparison, montmorillonite was formed in the upper part of the John Day Formation, where rainwater was supplied; and the minerals clinoptilolite, celadonite, and orthoclase were formed at depth, where the pH and ion concentrations had been raised by the solution and hydrolysis of glass.

Solution and hydrolysis of glass in the John Day Formation are indicated by several lines of evidence.

1. A pH of 8.5 was measured at room temperature in a slurry of finely ground rhyolitic glass from the ignimbrite of the John Day Formation. This pH presumably reflects the exchange of hydrogen ions for metallic cations (particularly

alkali ions) at the surface of vitric particles, which should occur in nature as well as in the laboratory (cf. Deffeyes, 1959, p. 607). This mechanism of ion exchange and its significance with reference to orthoclase are analyzed by Garrels and Howard (1959).

2. Diagenetic montmorillonite is abundant in the John Day Formation as a replacement of vitric material. Alteration of silicic glass to montmorillonite can be viewed as a hydrolysis reaction releasing silica and alkali ions into the solution.

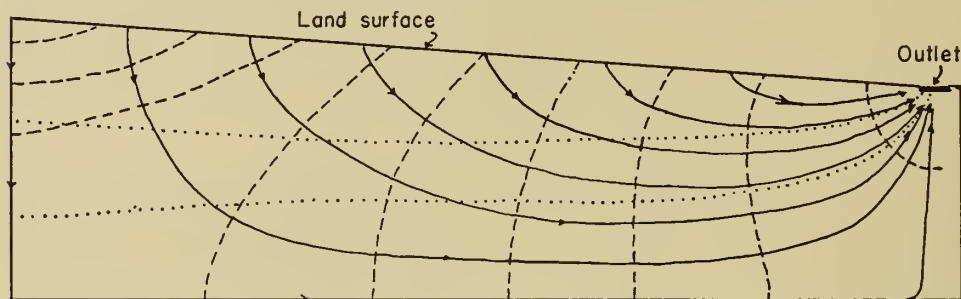


Fig. 10. Relation of isochemical lines (dotted) to subsurface flow lines (solid) and isopotential lines (dashed) beneath a gently sloping surface in rocks which are uniformly permeable except at base, where downward flow is limited by an impermeable horizon. It is assumed that (1) water is applied uniformly over surface; (2) water table lies at or near surface; (3) free flow prevails; and (4) change in chemical composition of the water is a function of the length of time the water is in contact with the rocks. This flow net was constructed graphically (cf. Taylor, 1948, pp. 161-166).

Any loss of alkali ions not compensated by a gain of other cations must involve an equivalent loss of anions—presumably oxygen, which increases the alkalinity as illustrated by the hydrolysis reaction $K_2O + H_2O \rightleftharpoons 2K^+ + 2(OH)^-$. Any replacement of metallic cations by hydrogen ions in forming montmorillonite must increase the pH and salinity as idealized by the reaction $K\text{-silicate} + H_2O \rightleftharpoons H\text{-silicate} + K^+ + OH^-$.

3. The complete solution of glass is abundantly demonstrated by etched shards in the fresh glass facies, by complete solution of shards at the margin of the clinoptilolite facies, and by petrographic evidence proving that most clinoptilolite replacing glass was deposited in cavities from which the glass had already been dissolved. Solution of glass would increase the pH as well as the concentration of ions, for the aluminosilicate species (or fragments) released into solution would hydrolyze, producing $Si(OH)_4$ (etc.) and free hydroxyl ions.

4. Finally, the alkali-rich, silicic mineral assemblage clinoptilolite-opal-orthoclase would be expected to crystallize in a solution of dacitic and rhyolitic glass.

FLOW PATTERN OF SUBSURFACE WATER

Assuming that the subsurface water progressively changed in composition with time, the older subsurface water should have had the highest pH and ion concentrations. The flow net of figure 10 illustrates the fact that if chemical composition of subsurface water is a function of time after infiltration, then the water composition varies directly with its depth in rocks of uniform permeability. In other words, the deeper subsurface water should have the higher concentration of dis-

solved ions—a fact recorded by Chebotarev (1955, pp. 138–145) for a number of areas. This relationship seems to account for the development of the clinoptilolite facies in the lower part of the John Day Formation.

The flow net of figure 10 was constructed graphically by the method described by Taylor (1958), and assumes free flow in rocks of uniform permeability, a water table at or near the surface, an impermeable horizon at the base, a uniformly sloping land surface, and uniform surface infiltration of water. To determine a horizon along which the water has the same age and presumably the same chemical composition, one needs to know the relative velocity of water moving along different flow paths and then compute the distance that water would flow down from the surface along these paths in a given period of time. Lines representing horizons of uniform age and composition (isochemical lines) are then drawn by connecting those points along flow lines where the water has moved for the same period of time after infiltration.

In order to compute the relative flow velocities and from these an isochemical line, one must first find the relative discharge rates of the arcuate flow paths between two flow lines. The discharge of each flow path is calculated by Darcy's law, $Q = KA H_1/L$, where Q is the rate of discharge (in volume per unit time), K the coefficient of permeability, A the average cross-section area, H_1 the head loss, and L the length of the flow path. For the two-dimensional flow net of figure 10, A is represented by the average width of the flow path, i.e., by the average distance between two flow lines.

If the rate of discharge is known, the average flow velocity for individual segments of a flow path bounded by two flow lines and two equipotential lines can be calculated from the relationship $V = Q/d_m$, where V is the velocity and d_m the average distance between two flow lines of a single flow segment (Todd, 1959, pp. 64–66). From the average velocity for each flow segment, one determines the distance that water travels along different flow paths in given lengths of time. The two isochemical lines were drawn in figure 10 by connecting those points along flow paths where the water has moved for two different periods of time after infiltration. These isochemical lines agree with the layering of ground water of different ages, determined by using tritium as a tracer in sandstones of New Jersey (Carlston *et al.*, 1961).

The principal conditions assumed for figure 10 probably represent, at least crudely, the actual conditions which prevailed in the John Day Formation during zeolitic diagenesis.

1. Free flow. The upper and lower members of the John Day Formation are quite similar in texture and appear to have equally low permeabilities except for differences produced by zeolitic diagenesis, thus indicating that free flow should have prevailed prior to zeolitic diagenesis. The fact that the surface of the clinoptilolite facies truncates folded beds of the formation suggests that water flowed across the bedding and was not confined to specific stratigraphic horizons. Flow across bedding also seems required to account for the extensive exchange of ions by rhyolitic and dacitic beds. Downward flow through the entire thickness of the formation is suggested by the abundant authigenic orthoclase in the lower 100 feet of the formation.

Local, rather small-scale departures from free flow are, however, suggested by field relationships in a few places. A devitrified welded tuff appears to have locally modified the subsurface flow in such a way as to prevent the alteration of an underlying bed of unwelded ignimbrite. The unwelded ignimbrite, 20–50 feet thick, contains fresh glass where it underlies 40 feet of welded tuff (fig. 8, sec. 2), but where the welded tuff pinches out, the unwelded ignimbrite is zeolitized. The welded tuff exhibits columnar jointing and probably constituted a permeable horizon, but it is not known how its permeability could have prevented the alteration of an underlying bed. Interfingering of the fresh glass facies with the clinoptilolite facies (fig. 5) may reflect differences in permeability. Here the more permeable beds are unaltered to greater depths than are the less permeable beds. This is to be expected, since water flows more rapidly in the more permeable beds, thus increasing the depth at which water of a given age and composition would be found.

2. Boundary conditions. Downward flow seems to have been limited by the weathered profile and colluvial claystones at the top of the Clarno Formation (see base of fig. 10), for authigenic celadonite seems to be absent in the upper part of the Clarno Formation, and authigenic orthoclase was found only in a hill of andesite which stands 300 feet higher than the nearby upper surface of the Clarno Formation (Hay, 1962a). It is not known whether the clinoptilolite in the upper 700 feet of the Clarno Formation should be attributed to the same water which accounted for zeolitic diagenesis in the John Day Formation. The water table should have been near the surface of the John Day Formation, for the rocks of the John Day Formation were of low permeability, and rainfall was at least 30 inches per year.

3. Topography. Configuration of the land surface at the time of zeolitic diagenesis is the most uncertain factor concerning the pattern of subsurface flow. If zeolitic diagenesis had been completed only a few thousand years prior to the extrusion of the Columbia River Basalt, the land surface may have resembled that which is now preserved at the base of the basalt flows. If so, the relief must have been somewhat less than the 1,000 feet exhibited by this buried surface, for the deepest valley at the base of the Columbia River Basalt appears to have been cut into the clinoptilolite facies after zeolitic diagenesis was completed. If zeolitic diagenesis preceded the basalt by several tens of thousands of years or more, the relief on the land surface might have been as little as 100 feet or possibly much more than 1,000 feet.

4. Conclusion. Free flow is the most important condition affecting the relation of water composition to depth, and wide differences in permeability along adjacent flow paths can reverse or otherwise modify the usual relationship. Within the John Day Formation, flow should have been free and unconfined. The slope and shape of isochemical lines (or surfaces) can be modified by changing the shape of the land surface, by the dimensions of the flow net, by the hydraulic gradient, or by allowing unrestricted flow at depth, but these changes do not modify the general relation of water composition to depth at any given location.

ORIGIN OF SHARP TRANSITION BETWEEN FACIES

The abrupt transition between beds containing fresh glass and those with clinoptilolite seems to signify a sharp change in water composition within the John Day Formation. Such a change in water composition induced purely by downward flow within the zone of permanent saturation is difficult to understand, however, for the water composition should have changed gradually along individual flow lines, and the change with depth should likewise have been gradational.

The sharp contact of the clinoptilolite facies with the fresh glass facies may have resulted from the migration of zeolitic diagenesis by way of an interface in which glass was totally dissolved. Clinoptilolite may have initially crystallized near the base of the formation, where the pH and ion activities were presumably highest. Once crystallization had begun, the solution would have become increasingly undersaturated with respect to glass, and the nearby vitric material should now have dissolved more rapidly, supplying ions to the solution and providing cavities for clinoptilolite. Crystallization of clinoptilolite would not have removed the hydroxyl ions produced in solution and hydrolysis of glass, and they would have maintained the pH at relatively high levels. A pH higher than 9 would probably have increased the solubility of glass, using as a model the solubility of silica and alumina in water. The solubility of silica at room temperature increases rapidly with rise of pH above 9 (Krauskopf, 1956); and the solubility of alumina—either as Al_2O_3 or $\text{Al}(\text{OH})_3$ —is almost negligible in pure water, but it increases rapidly above a pH of 9 (Correns, 1949). The solubility of aluminosilicate glass may well exhibit this same relation to a pH above 9.

Once started, the process seems to be potentially self-generating so long as glass is available and the solution moves slowly enough to become supersaturated in clinoptilolite as it passes along or through the zone where glass is dissolving. Thus it seems that the process can account for the complete replacement of glass by zeolite usually found in beds of the clinoptilolite facies.

If zeolitic diagenesis did move outward from one or more points of initial crystallization, the top of the clinoptilolite facies marks an isochemical surface generated by zeolitic diagenesis rather than by flow from above. Even if the chemical environment for zeolitic diagenesis was self-generated, however, zeolitization would be expected to advance more rapidly where the preëxisting subsurface water was most nearly appropriate for crystallization of clinoptilolite. Hence a self-generated surface of zeolitic diagenesis might be expected to parallel at least roughly the isochemical surfaces formed by flow from above.

According to the theory presented here, crystallization of clinoptilolite began when the depth of burial became great enough for the circulating water to reach the proper composition. Zeolitization may have ceased when erosion had reduced the thickness of the John Day Formation to a level at which the water no longer had a sufficiently high pH and concentration of ions. Increasing the hydraulic gradient by lowering the base level could have achieved the same result by increasing the flow rate to a point at which movement was too rapid for solution and hydrolysis of glass to supersaturate the solution in clinoptilolite.

The kinetics of nucleation may seem an alternative way of accounting for the

sharp contact of the fresh glass facies and the clinoptilolite facies, but this cannot be so. Many silicate reactions are sluggish at low temperatures, and one may wish to argue that clinoptilolite did not initially crystallize until the solution had become highly supersaturated with respect to this mineral. Once crystallization had begun, the early-formed clinoptilolite crystals seeded other crystals, thus allowing the surface of zeolitic diagenesis to advance by continuous nucleation into areas where the solution was barely saturated with respect to clinoptilolite. Conditions for the growth of clinoptilolite (but not for its spontaneous nucleation) may have been attained a few centimeters or a few tens of feet distant from preexisting clinoptilolite, but until seed crystals were available the clinoptilolite could not crystallize. This theory is invalidated by the fact that many samples of zeolitic claystone throughout the clinoptilolite facies contain isolated clinoptilolite replacements of glass separated from each other by montmorillonite clay. It is difficult to imagine how zeolite crystallizing in one cavity could nucleate clinoptilolite in an isolated cavity a centimeter away. It is more likely that the clinoptilolite nucleated spontaneously in the various cavities.

Nucleation of authigenic orthoclase by the plagioclase it replaces may, however, explain why orthoclase replacements of plagioclase are widespread, but orthoclase euhedra are restricted in the clinoptilolite facies. Replacement of plagioclase by orthoclase may have been essentially a process of ion exchange, for some elements of the original plagioclase lattices are preserved in much of the orthoclase. Selective replacement of the more calcic of the plagioclase crystals probably reflects their greater solubility or higher reaction rates at low temperatures. Diagenetic crystallization of vermiculite and kaolinite evidently required preexisting nuclei, for vermiform crystals of kaolinite occur only in beds containing finely divided detrital kaolinite, and vermiculite was formed only as an alteration of biotite or as an extension on altered biotite.

UNSOLVED PROBLEMS

The mechanism of zeolitic diagenesis proposed in this paper seems to account qualitatively for the salient features of the clinoptilolite facies, but leaves several problems unanswered.

1. It is not clear why abundant montmorillonite was formed at the advancing front of the clinoptilolite facies, where glass shards were being completely dissolved. The activity ratio of alkali ions to hydrogen ions was presumably higher at the advancing front of zeolitic diagenesis than elsewhere in the fresh glass facies; yet a low ratio of alkali ions to hydrogen ions should favor the leaching of glass to form a clay mineral. If, however, this montmorillonite was precipitated from solution rather than formed by leaching, then increased ion concentrations should have increased the amount of montmorillonite formed, up to the point where clinoptilolite crystallized. Petrographic evidence does not indicate whether the montmorillonite was formed by leaching or by precipitation from solution.

2. Anomalous beds with fresh glass in the clinoptilolite facies are a problem not explained by the self-generating mechanism proposed here, in which it is considered that zeolitic diagenesis can advance into areas where the pH and ion concentrations were too low for spontaneous crystallization of clinoptilolite. Per-

haps zeolitic diagenesis advanced independently from several horizons through the lower half of the formation, and the period of zeolitic diagenesis was too short for complete zeolitization of the lower member.

3. Differences in the redox potential adequate to account for the montmorillonite and celadonite subfacies cannot be satisfactorily explained on the basis of present information. Surface waters of differing Eh may have been supplied to different parts of the formation, or the Eh of the same mass of water may have been progressively lowered by oxidation of Fe^{+2} to Fe^{+3} in passing through the montmorillonite subfacies. In this hypothesis the celadonite subfacies should lie between the montmorillonite subfacies and the outlet for subsurface water. The pattern of subsurface flow and the distribution of the two subfacies are too poorly known to prove or disprove the latter hypothesis.

4. As yet there seems no satisfactory explanation for those mineralogic differences between the montmorillonite and celadonite subfacies which are unrelated to Eh, such as the apparent greater abundance of opal and of hollow pseudomorphs in the montmorillonite subfacies, and the more common occurrence of orthoclase pseudomorphic after plagioclase and the higher calcium content in clinoptilolite of the celadonite subfacies. One or more of these differences may not prove to be general when additional exposures of the clinoptilolite facies are examined in detail.

COMPARISON WITH OTHER EXAMPLES OF ZEOLITIC DIAGENESIS

The literature on zeolites in sedimentary rocks has been summarized by Coombs *et al.* (1959) and Deffeyes (1959); hence only examples in which low-temperature zeolitic diagenesis can be related to water composition will be presented here. These occurrences show that zeolitics are characteristically formed at low temperatures in solutions in which the ratio of alkali ions to hydrogen ions is high, a fact Hemley (1961) also found to be true at a temperature of 200°C in the laboratory.

1. Phillipsite has long been known to occur in sea-floor sediments, where it formed as an alteration product of volcanic glass (Murray and Renard, 1891).

2. Ross (1928, 1941) noted volcanic glass replaced by analcite in the deposits of a playa lake in Arizona, for which a saline water composition seems probable.

3. Analcite and apophyllite occur as alteration products of volcanic glass at a number of horizons in the Green River formation of Utah, Wyoming, and Colorado (Bradley, 1929). Crystal molds of glauberite and anhydrite were noted by Bradley at many horizons in the formation, and a variety of sodic carbonates (e.g., trona, nahcolite, shortite) has since been reported (Milton and Eugster, 1959). The analcite and apophyllite were thought to have formed on the lake bottom by reaction of alkaline lake water with dissolution products of volcanic ash that fell into the lake (Bradley, 1929).

4. Analcite and heulandite were found in cores of Pliocene (?) lake beds near Kramer, California, by Benda *et al.* (1960). The borate minerals veatchite and colemanite were noted over part of the same core interval as the zeolites, and halite and borax were present in the water-soluble fraction of one sample containing analcite.

5. Zeolites and opaline material are present in Pleistocene sedimentary rocks of Danby and Cadiz dry lakes of California (Droste, 1961). Gypsum, halite, and bassanite were identified in cores from both of these lakes by Basset *et al.* (1959).

6. R. J. Moiola and the present writer have identified authigenic zeolites and potash feldspar in the U. S. Geological Survey cores of late Pleistocene sediments from Searles Lake, California. Analcite is recognizable in diffractometer patterns from 19 of the 72 samples studied. Authigenic potash feldspar was identified in 36 of the samples, and phillipsite in 3 of them. Only the phillipsite is restricted to tuffs, which constitute no more than a few feet of the cored sequence, which is 875 feet thick. Droste (1961) could find no evidence in these cores that clay minerals have been formed in Searles Lake. Evaporates which include a variety of sodium carbonate minerals occur throughout the core (Smith and Pratt, 1957; Haines, 1959); and the tuffs must have altered in concentrated brine, whether on the lake floor or after burial. The brine in the uppermost salt bodies has a pH of 9.1–9.4 (Haines, 1959, p. 146), and the saline mineral assemblage indicates that the water should be alkaline at depth.

7. Moiola and the writer have found erionite of authigenic origin to be the principal constituent of tuffaceous layers interbedded with trona in core samples from depths of 7–173 feet in the late Pleistocene and recent sediment of Lake Magadi, Kenya (Baker, 1958). Phillipsite and clinoptilolite (or heulandite) can be recognized in diffractometer patterns of a few samples. A saturated solution of trona in equilibrium with the atmosphere has a pH of 10.0 as measured in the laboratory, thus indicating the probable alkalinity at which the zeolites were formed.

SUMMARY OF CONCLUSIONS

1. The John Day Formation comprises two sharply separated mineralogic facies. Clinoptilolite replaces vitric material in most claystones and tuffs of the lower half of the formation to form a *clinoptilolite facies*, and fresh glass is present and zeolite lacking in the upper part of the formation, which constitutes a *fresh glass facies*. On the basis of clay-minerals content the clinoptilolite facies can be subdivided into a montmorillonite subfacies and a laterally equivalent celadonite subfacies.

2. Zeolitic diagenesis occurred in the Miocene between the time the John Day Formation was folded and the Columbia River Basalt was deposited. Most or all of the zeolitic diagenesis was accomplished at burial depths of 1,250–4,000 feet.

3. Opal, orthoclase, and celadonite were locally co-precipitated with clinoptilolite. Nearly all the montmorillonite preceded the zeolite with which it is associated, as most of the celadonite may have done, but nearly all the calcite was deposited after the zeolite.

4. Replacement of rhyolitic glass by clinoptilolite involved a gain of H₂O, Ca, and Mg, and a loss of Si, Na, K, and Fe. Altered rhyolitic rocks of the clinoptilolite facies lost alkalis and gained Fe, Ti, Mg, Ca, and less commonly P. Silica remained constant in some rocks, but was lost from the others. Some at least of the dacitic rocks have gained K and Si, and losses of Fe, Ti, Mg, Ca, and P can be inferred. The chemical similarity of altered rhyolitic and dacitic rocks suggests that ions were exchanged by these beds in the alteration process.

5. The two diagenetic facies of the John Day Formation are probably a result of leaching in an open system. Montmorillonite was formed in the upper part of the formation, where rainwater was supplied, and the minerals clinoptilolite, celadonite, and potash feldspar were formed at depth, where the pH and ion concentrations had risen to relatively high levels through the solution and hydrolysis of glass.

6. A self-generating mechanism involving the interdependent solution of glass and the precipitation of clinoptilolite seems to be the most satisfactory way to explain the sharp contact between the two facies and the complete zeolitic replacement of glass in most beds of the clinoptilolite facies.

7. Several examples are given in which zeolites can be shown to form in moderately or strongly saline solutions having an alkaline pH. These examples support the writer's suggestion that the clinoptilolite of the John Day Formation crystallized from ground water having a high ratio of alkali ions to hydrogen ions.

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PLATES

PLATE 1

Zeolitized vitric tuff of montmorillonite subfacies showing poorly sorted vitric particles replaced by clinoptilolite in a matrix of montmorillonite. Length of bar 0.5 mm.



PLATE 2

a. Partly dissolved glass shards (Gl) and pseudomorphic cavities (Cv) in transition zone between fresh glass facies and clinoptilolite facies. Original shapes of cavities preserved by matrix of montmorillonite. Length of bar 0.5 mm.

b. Hollow clinoptilolite pseudomorph of vitric particle in tuff of montmorillonite subfacies. Crystals of clinoptilolite (Cl) form margin enclosing unfilled central cavity (Cv). Pseudomorph enclosed by matrix of vitric material replaced by clinoptilolite and montmorillonite. Length of bar 0.5 mm.

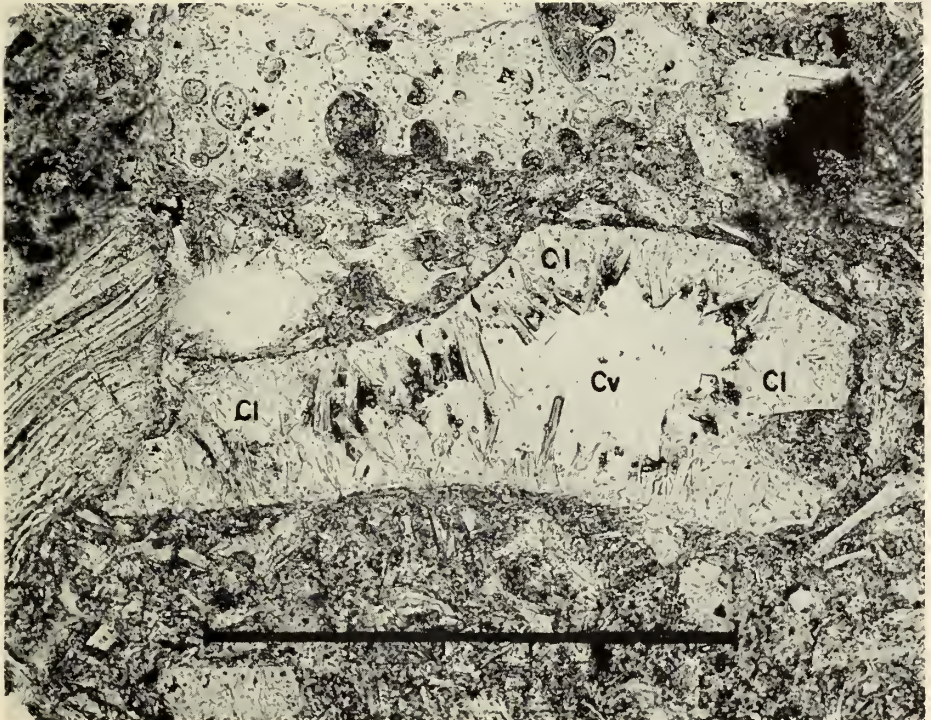
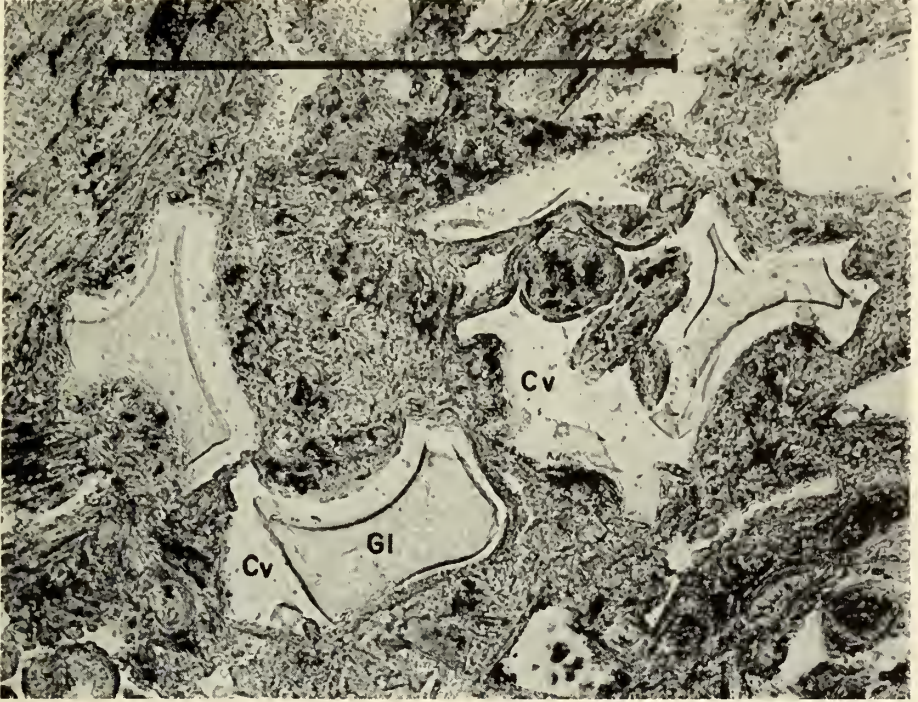


PLATE 3

a. Opal and clinoptilolite pseudomorphic after shards of irregular shape in zeolitized ignimbrite of celadonite subfacies. Lower, early-deposited half of both pseudomorphs comprises outer thin margin of clinoptilolite (Cl) and inner filling of opal (Op). Upper half of both pseudomorphs consists of clinoptilolite (Cl). Pseudomorphs are enclosed by vitric material replaced by clinoptilolite, clay minerals, and opal. Length of bar 0.5 mm.

b. Vesicular particle of glass replaced by opal, clinoptilolite, and montmorillonite in zeolitized ignimbrite of celadonite subfacies. Montmorillonite (Mt) lines original vesicles and fills a fracture. Opal (Op) is concentrated in bottom of pseudomorph, where it replaces glass and fills vesicles; it forms a thin coating inside edge of a vesicle (Cv) in upper half of pseudomorph, where clinoptilolite (Cl) replaces glass. Montmorillonite was deposited before glass was dissolved; opal and clinoptilolite were deposited after solution of glass. Vitric material replaced by clinoptilolite and clay minerals forms matrix of pseudomorph. Length of bar 0.5 mm.

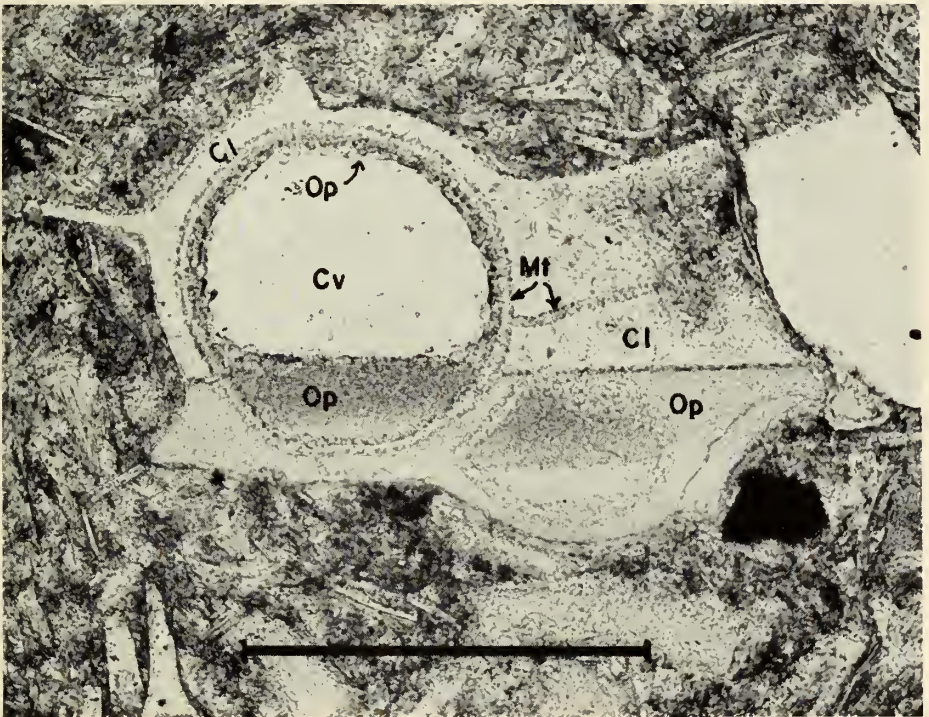
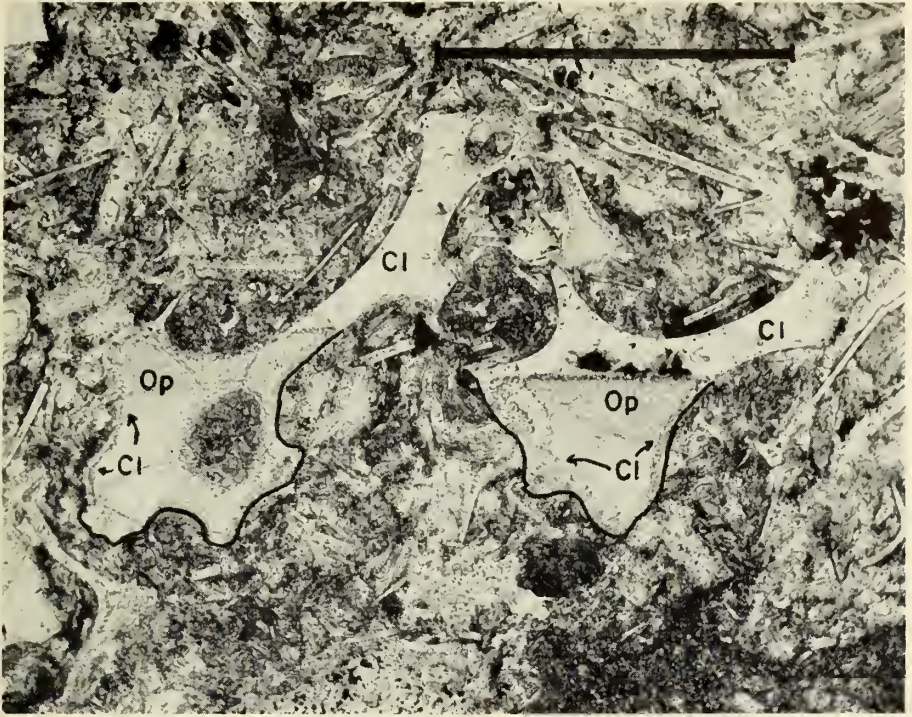


PLATE 4

a. Clinoptilolite-montmorillonite pseudomorph of angular fragment of glass in a zeolitized tuff of montmorillonite subfacies. Montmorillonite (Mt) forms a boxwork filled with crystals of clinoptilolite. Pseudomorph is enclosed by a matrix of vitric material replaced by clinoptilolite and montmorillonite. Length of bar 0.5 mm.

b. Clinoptilolite pseudomorphic after obsidian in zeolitized ignimbrite of montmorillonite subfacies. Original welded-tuff texture of obsidian is perfectly preserved by banding of ferric oxide dust in lower half; preservation of texture is imperfect in upper half. Length of bar 0.5 mm.

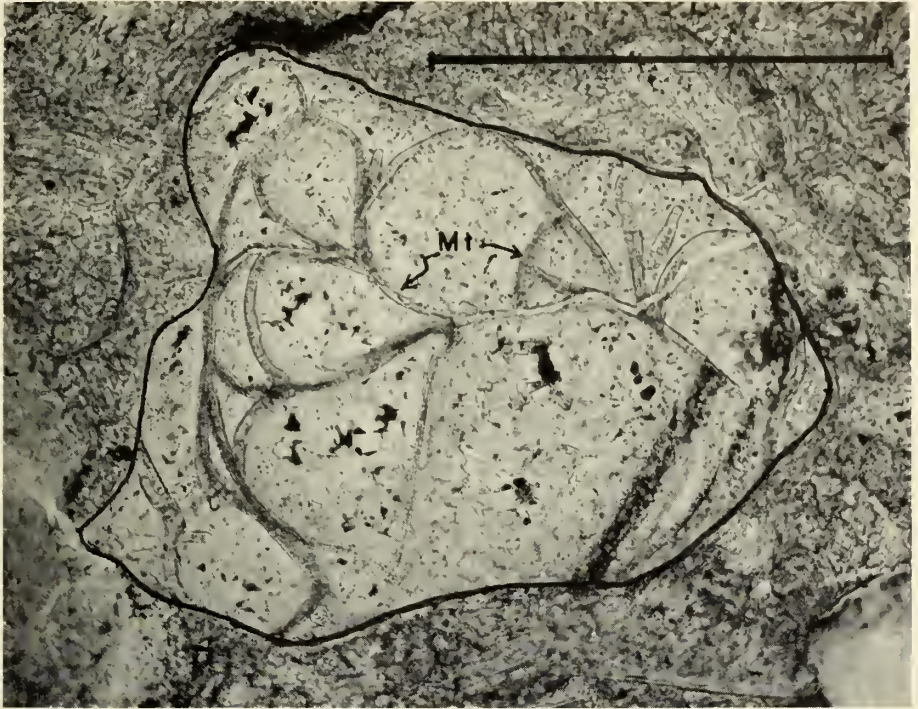
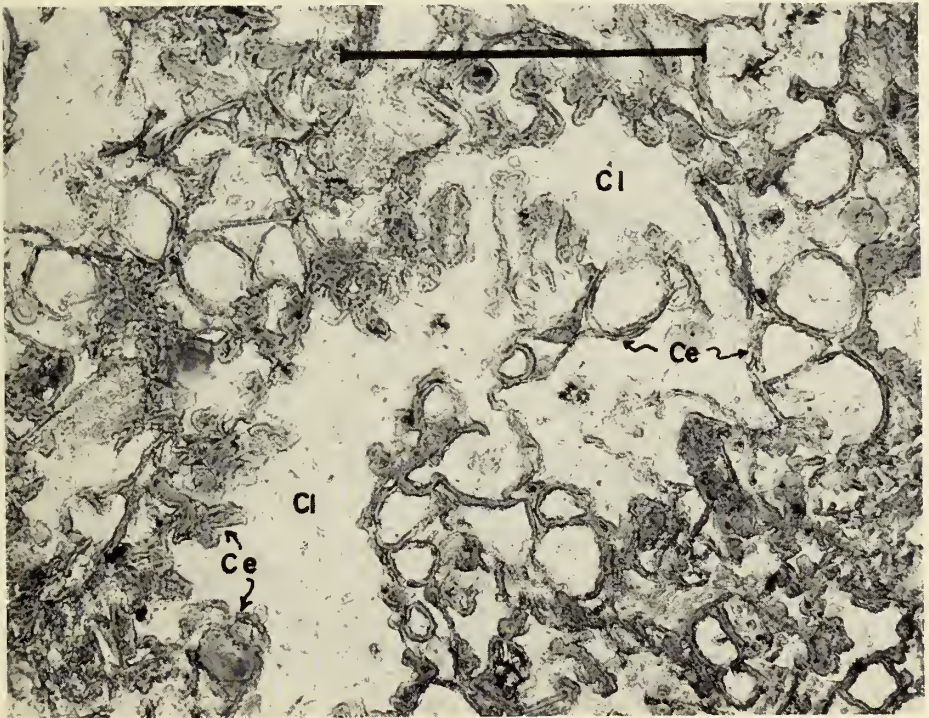
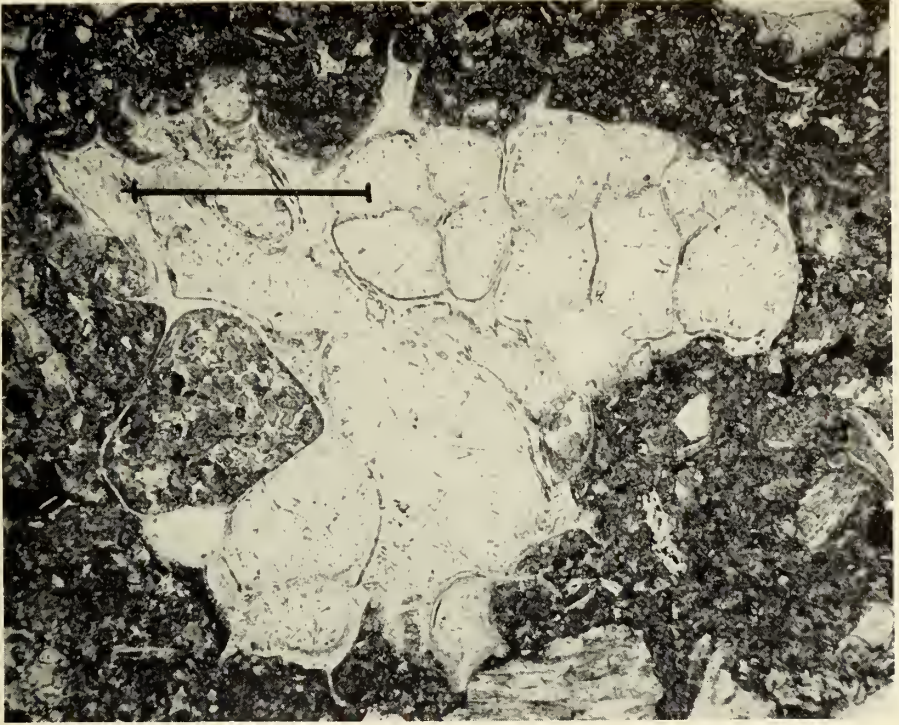


PLATE 5

a. Clinoptilolite replacement of a pumice fragment in zeolitized tuff of celadonite subfacies. Clinoptilolite fills vesicles and replaces glass of pumice fragment, which is enclosed by a matrix of montmorillonite and celadonite. Length of bar 0.5 mm.

b. Pumice replaced by clinoptilolite (Cl) and celadonite (Ce) in core of a celadonitic concretion in zeolitized ignimbrite of celadonite subfacies. Original texture of pumice highly disrupted. Length of bar 0.5 mm.





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R 20 E | R 21 E

120° 45'

R 21 E | R 22 E

R 22 E | R 23 E

Spray 12 mi.

GEOLOGIC MAP
OF
AN AREA NORTH OF MITCHELL,
WHEELER COUNTY, OREGON

BY
R.L. HAY, 1961

119° 45'

T 9 S
T 10 S

44° 45'

T 9 S
T 10 S


① Location of measured section:
Bar (—) indicates area(s) at
measurement in extended
sections.

 Alluvium (Quaternary)

 Landslides (Quaternary)

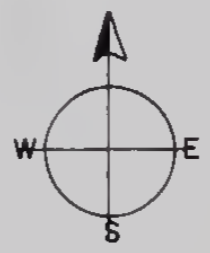
 Columbia River basalt (Miocene)

 Ignimbrite forming middle member
of John Day formation.

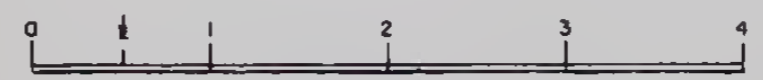
 John Day formation (undivided)
(Oligocene - Miocene)

 Clarno formation (Eocene)

 Cretaceous rocks



SCALE OF MILES



120° 45'

R 20 E | R 21 E

Mitchell 4 mi.

To accompany Richard L. Hay, "Stratigraphy and Facies Development of the John Day Formation of Oregon," Univ. Calif. Publ. Geol. Sci. Vol. 42, No. 3.

Fig. 2 Geologic map of area north and northeast of Mitchell, Oregon. Part of geology in Donnelly Basin taken from Lindsay (1961); all other mapping is that of Hay.



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6

S. edge SW 1/4 Sec. 7
T10S, R21E







9

SW 1/4 Sec. 31
T10S, R21E
NE 1/4 Sec. 36
T10S, R20E



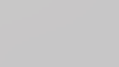
14 + 15

NW 1/4 Sec. 22
SE 1/4 Sec. 21
T10S, R22E

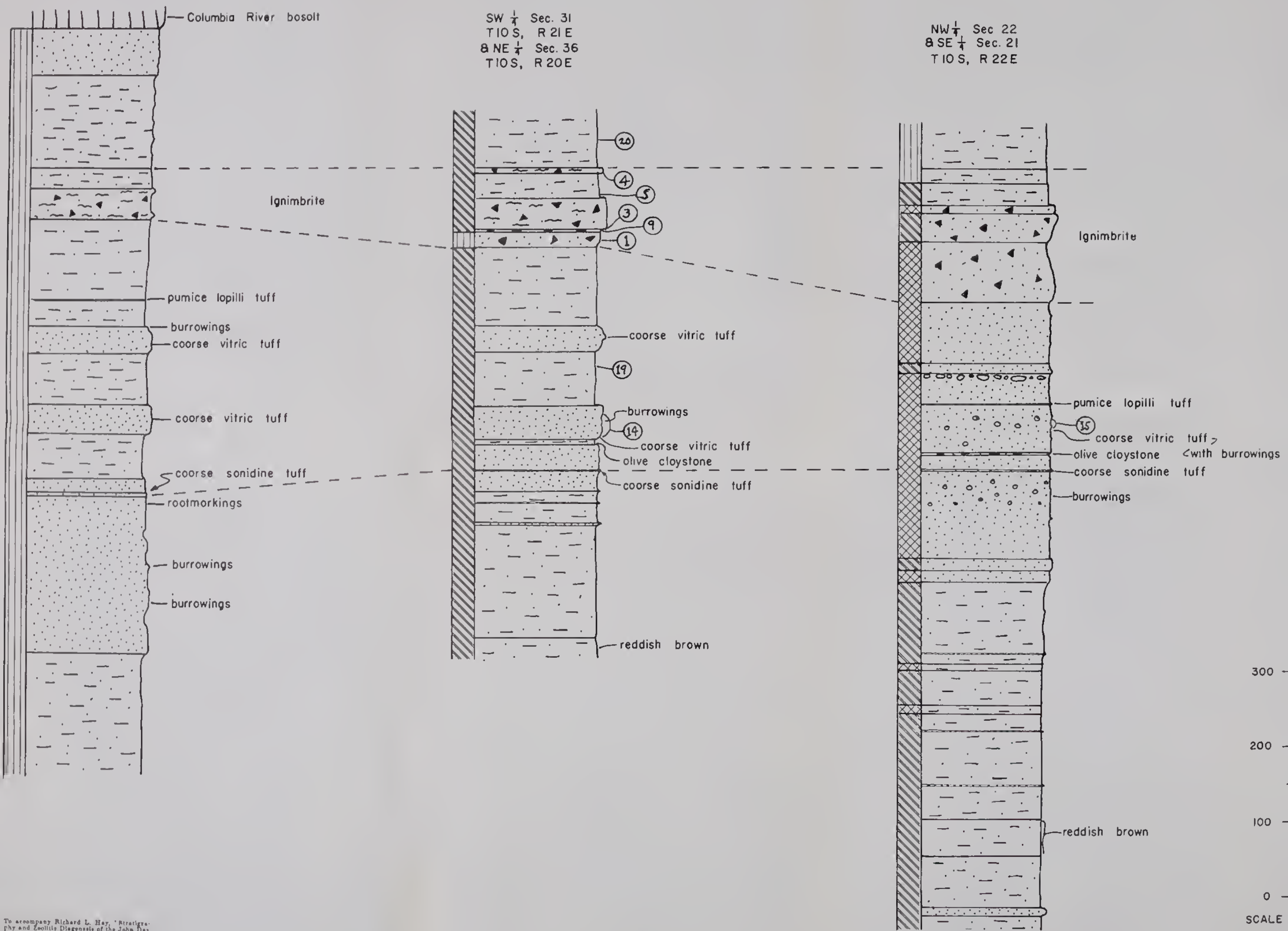
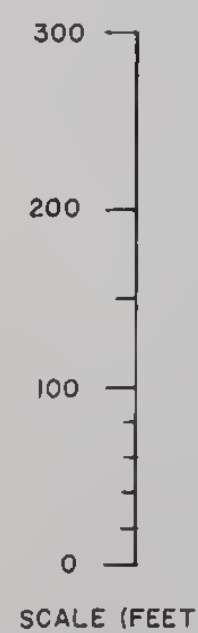
EXPLANATION

-  Columbia River basalt
-  Welded and semi-welded tuff
-  Unwelded lapilli tuff
-  Tuff
-  Tuffaceous claystone
-  Coloreous concretions

JOHN DAY FORMATION

-  Fresh glass facies (dominantly yellowish gray)
-  Montmorillonite subfacies of clinoptilolite facies (claystones dominantly dusky yellow, tuffs dominantly yellowish gray)
-  Celadonite subfacies of clinoptilolite facies (dominantly grayish green)

① Location of specimen chemically analyzed; numbers correspond to table

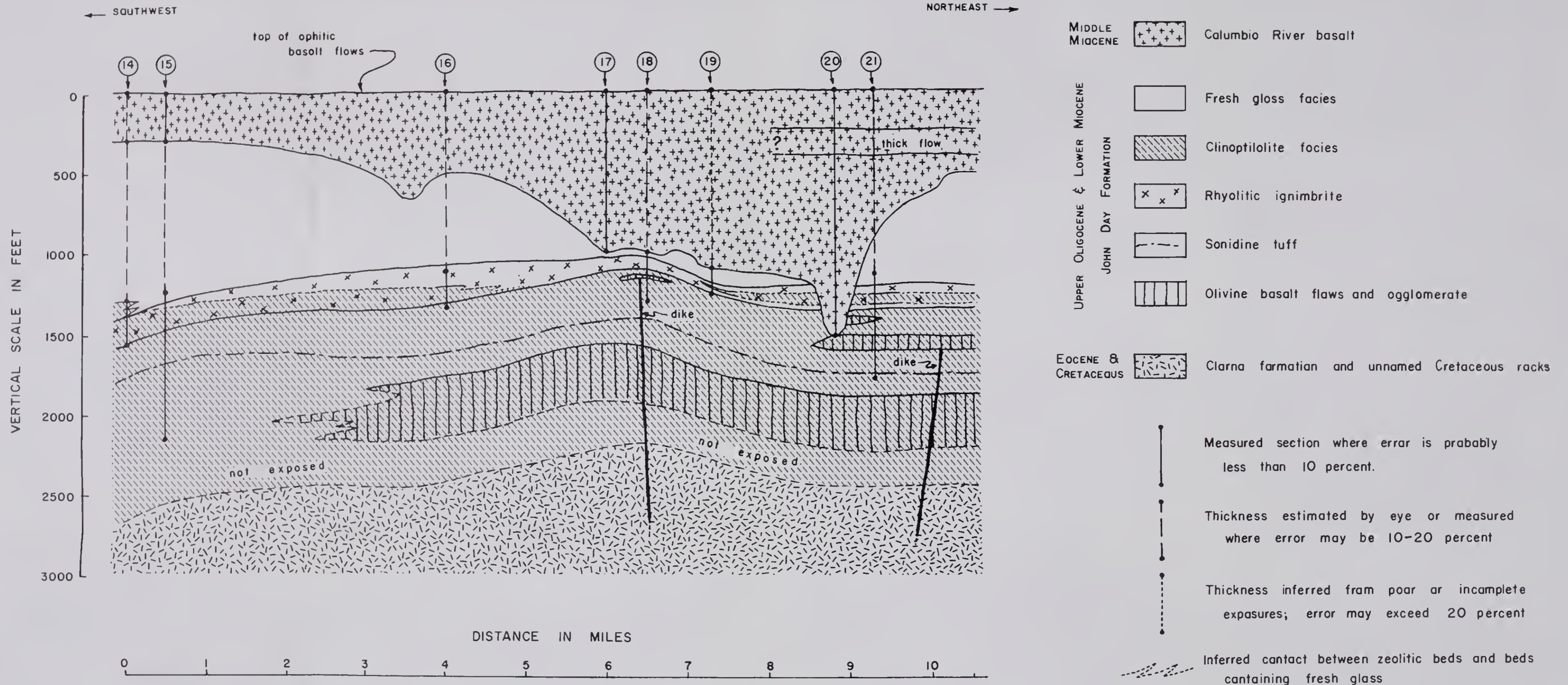


To accompany Richard L. Hay, "Stratigraphy and Zeolite Diagnosis of the John Day Formation of Oregon," Univ. Calif. Publ. Geol. Sci., Vol. 45, No. 3.

Fig. 8. Columnar sections of exposed parts of the John Day Formation near Mitchell, Oregon, representing different diagenetic facies. Section numbers correspond to those of stratigraphic sections in figs. 2, 4, and 5. Only upper 120 feet of column at right represent sec. 14; remainder represents sec. 15.

STRATIGRAPHIC SECTIONS (NUMBERS 14-21)

EXPLANATION



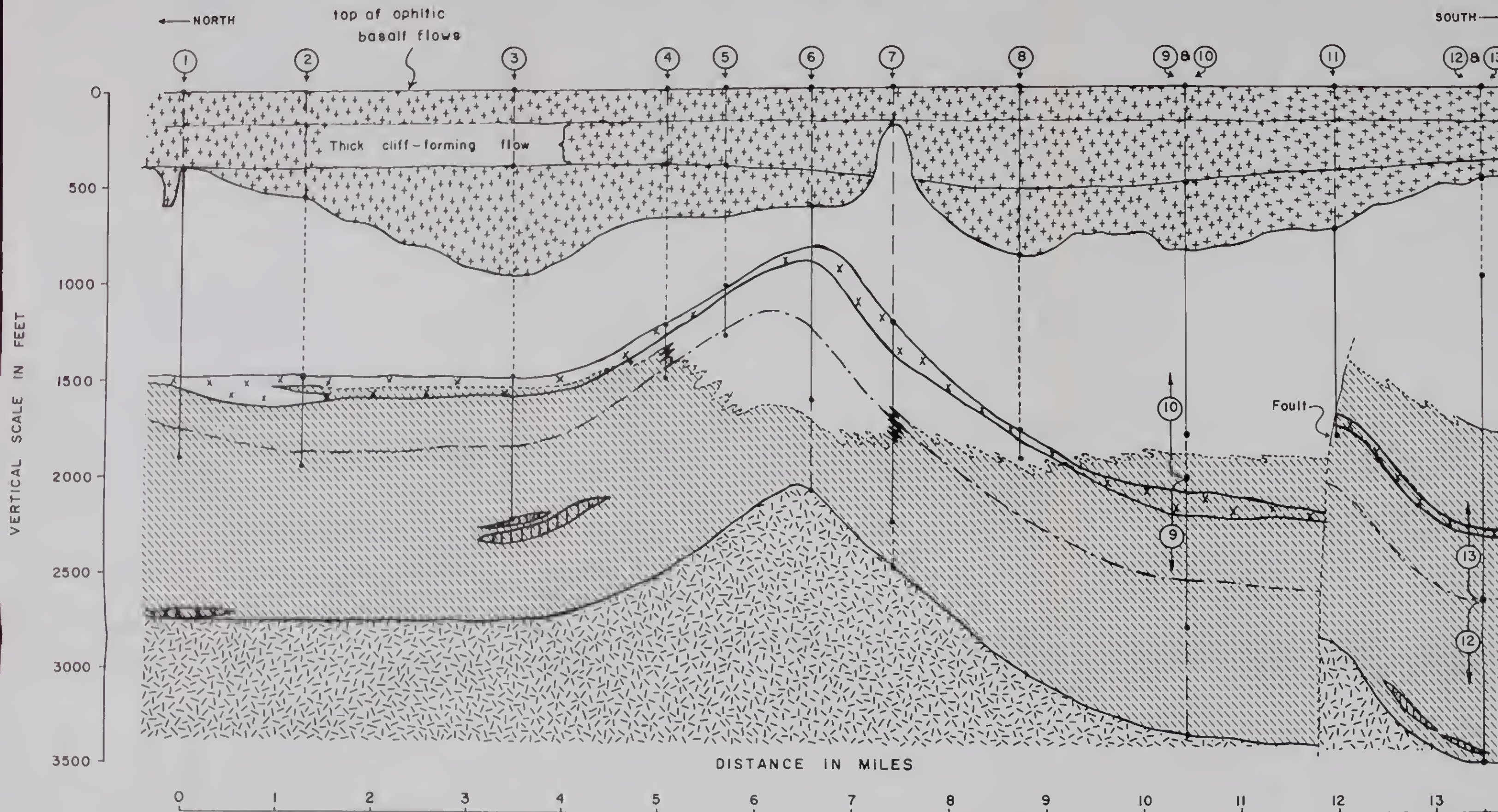
(Approximately 10:1 vertical exaggeration)

To accompany Richard L. Hay, "Stratigraphy and Zeolitic Diagenesis of the John Day Formation of Oregon," Univ. Calif. Publ. Geol. Sci., Vol. 42, No. 5.

Fig. 5. Pattern of zeolitic diagenesis within the John Day Formation northeast of Mitchell, Oregon. Based largely on stratigraphic sections depicted in fig. 2. Although the Columbia River Basalt has been folded in this area, the top of the ophitic flows is shown as a horizontal plane.

STRATIGRAPHIC SECTIONS (NUMBERS 1-13)

EXPLANATION



- MIDDLE MIOCENE
 - Columbia River basalt
- UPPER OLIGOCENE & LOWER MIOCENE JOHN DAY FORMATION
 - Fresh glass foci
 - Clinaptillolite foci
 - Rhyolitic ignimbrite
 - Sanidine tuff
 - Olivine basalt flows and agglomerate
- Eocene
 - Clarno formation

- Measured section where error is probably less than 10 percent.
- Thickness estimated by eye or measured where error may be 10-20 percent.
- Thickness inferred from poor or incomplete exposures; error may exceed 20 percent.
- Inferred contact between zeolitic beds and beds containing fresh glass.
- Observed contact between zeolitic beds and beds containing fresh glass.

(Approximately 10:1 vertical exoggeration in scale)

Fig. 4. Pattern of zeolitic diagenesis within the John Day Formation north of Mitchell, Oregon. Based largely on stratigraphic sections depicted in fig. 2. Although the Columbia River Basalt has been gently warped, the top of the ophitic flows is shown here as a horizontal plane. The fault shown in sec. 11 appears to postdate the Columbia River Basalt.

To accompany Richard L. Hay, *Miscellaneous Publications and Zeolitic Diagenesis of the John Day Formation of Oregon*, Univ. Calif. Publ. Geol. Sci., Vol. 42, No. 5

